Doctoral Dissertation

博士論文

ASSESSMENT OF TRACE METALS IN THE ENVIRONMENTAL MEDIA AND FOODS FROM THREE RIVERS AND THEIR ADJACENT AREAS IN DHAKA CITY, BANGLADESH

バングラデシュ、ダッカ市の三つの河川とその周辺地域における環境媒体と食品に含まれる微量金属の評価

By

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List of Abbreviations and Acronyms

ASV	Average Shale Value
ATSDR	Agency for Toxic Substance and Disease Registry
BSAF	Biota Sediment Accumulation Factor
CRM	Certified Reference Materials
DoF	Department of Fisheries
DEPZ	Dhaka Export Processing Zone
DW	Dry weight
DWSB	Drinking water standard Board
DU	Dhaka University
EC	Electrical Conductivity
E-waste	Electronic waste
FW	Fresh weight
HI	Hazard Indices
HQ	Hazard Quotients
ICP-MS	Inductively Coupled Plasma Mass spectrometer
IQCs	Internal Quality Controls
LEL	Lowest Effect Level
PM	Particulate Matter
PSTU	Patuakhali Science and Technology University
PTFE	Polytetrafluoroethylene
RDA	Recommended Dietary Allowance
RSD	Relative Standard Deviation
SEL	Severe Effect Level
SLER	Sustainable Living with Environmental Risk
TF	Transfer Factor
THQ	Target Hazard Quotients
TRV	Toxicity Reference Value
UCC	Upper Continental Crust
USDOE	United States Department of Energy
UNDP	United Nations Development Program
UNEP	United Nations Environment Program
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
YNU	Yokohama National University

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Abstract of thesis

Trace metal is a member of loosely defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Trace metals are ubiquitous in the environment, as a result of both natural and anthropogenic activities. They are stable and cannot be destroyed, and therefore tend to accumulate in the environment. In recent years, there has been a substantial concern over the extent of contamination of the environment with toxic elements and their involvement to public health. Therefore, the accumulation of trace metals in the environment cause a potential risk to human health due to their transfer, uptake by flora and fauna and subsequent introduction into the food chain.

In this thesis, trace metals like chromium, nickel, copper, arsenic, cadmium and lead were investigated in the environmental media and commonly consumed food composites around three riverine ecosystems in Dhaka City, Bangladesh. Dhaka is one of the ten mega-cities in the world. The population of Dhaka City is predicted to increase about 21 million by 2020 from the current population of 12 million. With the rapid development, this city is facing numerous environmental challenges. The distribution of trace metals in the terrestrial and aquatic environment, as well as their impact upon organisms and human health, are of great concern due to their persistent, non-biodegradable and toxic properties. To date, there have been a few studies on trace metal monitoring in Bangladesh and data on the distribution of trace metals in the urban riverine ecosystems are scarce. In addition, there have been no investigations on the chemical speciation of trace metals in soil and sediments. The principal aim of this thesis, however, was to investigate the levels of trace metals in the environment and assess human health risk due to metal exposure.

Wide-scale monitoring campaign of trace metals were undertaken simultaneously besides three riverine ecosystems between 21st February and 26th March 2012 (winter) and 4th August and 8th September, 2012 (summer). Further monitoring was completed in the same study area at summer (10th August – 17th September, 2013) to analyze the seasonal variation of these contaminants. There were nine monitoring sites from three different rivers (Turag, Buriganga and Shitalakha) around Dhaka City, Bangladesh.

Considering the data from all sites of three rivers, total concentrations of metal in water were 31±32, 16±4.4, 22±8.3, 19±3.8, 0.29±0.07 and 4.7±2.0 µg/L in winter and 23±27, 22±7.4, 11±3.7, 11±3.0, 0.24±0.06 and 3.5±1.5 µg/L in summer for Cr, Ni, Cu, As, Cd and Pb,

respectively. During winter season, total concentrations of metal in sediment were 844±638, 411±102, 251±93, 42±8.2, 19±4.7 and in summer 385±567 mg/kg dw and 547±581, 298±121, 130±52, 27±12, 16±6.1 and 327±560 mg/kg dw for Cr, Ni, Cu, As, Cd and Pb, respectively for all sites of three rivers. Elevated concentration of Cr was found at B1 site of Buriganga River (close to the tannery industry) and Pb was found at B2 site of Buriganga River (close to the lead smelting factory). Sequential extraction tests revealed that the studied metals were predominantly associated with the residual fraction, followed by the organically bound phase. The concentrations of these metals in water and sediment varied seasonally, where winter season showed higher than summer. Slightly higher levels of metals during winter might be attributed to the variation in water capacity of the river, where water input to the river is generally limited in winter, resulting in the precipitation of pollutants in water and sediment.

The concentrations of Cr, Ni, Cu, As, Pb and Cd in eight different land use soils (total of 70 sampling sites) were in the range of 2.4–1258, 8.3–1044, 9.7–823, 8.7–277, 1.8–80 and 13–842 mg/kg, respectively which exceeded the environmental action level for soils. Among the land-use types, tannery waste disposal site (TW) appeared the most impacted with trace metals. The concentrations of metal were subsequently used to establish hazard quotients (HQs) for the group specific population through ingestion, dermal contact and inhalation pathways.

In this study, the levels of trace metals in eight categories of foods (n=173) were also investigated, namely, cereals, pulses, vegetables, fruits, fish, meat, egg and milk which were collected from study sites like agriculture field, household, adjacent river (Turag, Buriganga and Shitalakha) and local market in Dhaka City. The mean concentrations of Cr, Ni, Cu, As, Cd and Pb in cereals (1.8, 1.3, 2.3, 0.64, 0.075 and 0.17), pulses (1.9, 1.9, 4.0, 0.24, 0.018 and 0.35), vegetables (0.68, 3.2, 12, 0.083, 0.15 and 0.84), fruits (1.4, 1.2, 5.4, 0.38, 0.04 and 0.53), fish (2.4, 1.6, 3.7, 0.25, 0.035 and 1.0), meat (1.3, 0.60, 2.1, 0.037, 0.027 and 0.25), egg (1.4, 1.9, 4.0, 0.087, 0.022 and 0.24) and milk (1.6, 1.5, 2.3, 0.056, 0.029 and 0.20 mg/kg fresh weight). The mean concentration of Cr, Ni, As, Pb in most of the food samples were higher than the maximum allowable concentration (MAC), indicating these foods are contaminated by these metals. Trace metals in water, soil and foods were exceeded the international standard levels. It is assumed two possible ways for the relationship of metal transformation to food. Firstly, soils are contaminated by the inclusion of trace metals through the industrial waste. Consequently, the foods which are grown in these land area are highly contaminated by trace metals. Secondly, river water which is contaminated through the

industrial effluents are using for irrigation in the adjacent agricultural land. This might have some relations for the metal contamination in foods that are grown in the study area.

In the study area, local people might expose trace metals through three possible exposure media such as foods, water and soil. The daily intake (EDI) of Cr, Ni, As, Cd and Pb through the exposure media were higher than the maximum tolerable daily intake (MTDI) indicating an obvious health risk. This study highlights the importance of site specific multipathway health risk of the urban people regarding trace metals exposure in the capital city of Bangladesh.

Chapter 1

GENERAL INTRODUCTION

General Introduction

1.1   Trace metals in the environment

The term "trace metals" has been often used in the literature of environmental pollution as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or eco-toxicity. A trace metal is a metal of relatively high specific gravity greater than 5 or high atomic weight (Csuros et al., 2002). Metals and metalloids occur naturally in the Earth's crust, and are released to soils and the hydrological cycle during physical and chemical weathering of igneous and metamorphic rocks. The contamination of water, sediment, soil and foodstuffs by trace metals is of major concern in many developing countries like Bangladesh, because of their toxicity, persistence and bio-accumulation. In developing countries, industrial activities such as metal work-shops, battery manufacturing industries, tanneries, pharmaceuticals and other factories produce huge volumes of effluents that contain trace metals and other toxicants, which adversely affect on the invertebrates, fish, vegetables and humans (Uluturhan and Kucuksezgin, 2007; Tiwari et al., 2008). In Bangladesh, everyday huge amounts of untreated industrial waste have been discharged into open water bodies and its adjacent lands. Besides, a considerable amount of suspended materials having trace metals coming down from neighboring country like India through the Teesta and the Brahmaputra Rivers which can be strongly accumulated in water, sediment and food chain (Megeer et al., 2000; Jones et al., 2001; Almeida et al., 2002; Xu et al., 2004). Although analyses of trace metals in sediments have been used extensively for the monitoring study (Pekey et al., 2004; Liu et al., 2007), few researchers have focused on the routes of transmission of metals from sediment to fish and finally to humans.

Polluted river water is mostly used for the irrigation of crops in the urban areas due to freshwater shortage. Generally, wastewater irrigation is responsible for soil contamination with trace metals which further lead to contaminate the food crops. It is a fact that trace metals have adverse impact on soil ecosystem and lead to human health risks. In the vicinity of urban riverine ecosystems, the primary pathways of metal accumulation in humans are through the ingestion of contaminated drinking water, foods and soil. Therefore, the food chain contamination is the major pathway of trace metal exposure for humans (Khan et al., 2008).

Trace metals in contrast to most pollutants, not bio-degradable, and they undergo a global ecological cycle in which natural water are the main pathways. The inorganic

pollutants especially trace metals are the greatest concern due to their persistence in the environment and later become a potential source of risk to the nearby soil and vegetation. Different kinds of foods are grown during the year in the river watershed area, Bangladesh but very little is known about the metal contents of local foods. Indeed, there have been some studies on the monitoring of trace metals in Bangladesh, but no reported studies on the possible health risks associated with the consumption of contaminated foods and exposure from the polluted urban soils of different land use.

1.2　Study Framework

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            ┌─────────────────────────────────────┐
            │  Toxic metals (Cr, Ni, Cu, As, Cd and Pb)  │
            └─────────────────────────────────────┘
                              │
            ┌─────────────────────────────────────┐
            │   Urban river and their adjacent area    │
            └─────────────────────────────────────┘
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      ┌──────────┬──────────┬──────────┬──────────┐
   ┌──────┐  ┌────────┐  ┌──────┐      ┌────────────┐
   │ Water │  │Sediment│  │ Soil │      │ Food stuffs │
   └──────┘  └────────┘  └──────┘      └────────────┘
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Water / Sediment	Soil	Food stuffs
Monitoring and assessment of trace metals in the aquatic environment	Monitoring of trace metals in soils of different land use	Monitoring of trace metal contamination in different foods
	Health risk assessment due to metal exposure from soil through ingestion, dermal contact and inhalation	Assessment of health risk due to consumption of foods

To understand the present environmental state of trace metals in both terrestrial and aquatic environment with the view to address environmental problems in the urban area of Dhaka City, Bangladesh

1.3　Problems statement of the study area

The Dhaka, capital of Bangladesh is one of the most densely populated cities in the world, home to approximately twelve million people of which less than 25% are served by sewage treatment facility (Ahmad et al., 2010). In the last decade's natural and human activities driven changes the peripheral rivers of Dhaka City and caused a complete deterioration of water quality. The river Buriganga is increasingly being polluted with the city's thousands of industrial units and sewerage lines dumping huge volumes of toxic wastes

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into it (Mohiuddin et al., 2011; Islam et al., 2006). The unpleasant odor of the polluted black water of Buriganga, Turag and Shitalakha River can be sensed even from half a kilometer distance. Intensive human intervention, unplanned urbanization and population pressure have created the present unwanted situation of these rivers (Mohiuddin et al., 2011). Many industries have set up in and around the city during the last decade, and the number of new industries are continually increasing. Tannery and other auxiliary industries, including 73 glue and paint industries, 273 tanneries and other industries discharge effluents 504,000 m^3/year into the surrounding rivers and canals, thereby, increasing the level of pollutants (Asaduzzaman et al., 2002). Thus, ecotoxicological risks posed by the effluents from tanneries and other industries cannot be overemphasized. However, little attention is given to the environment, health and sanitary conditions around the vicinity of these industries.

Trace metals in the environment can originate directly from industrial activities, traffic emissions, brick kilns, municipal waste, and domestic activities. Indiscriminate use of inorganic fertilizer and chemicals in agricultural field are responsible for accumulation of trace metals in the environment (Ahmad et al., 2010). Very few studies stated the problems of trace metals in Bangladesh. Recently no fish and aquatic organisms found in the rivers around Dhaka City. Ground water table is depleted due to over withdrawn of water that may jeopardize its lives and development which is the crucial issue to diversify the sources of water supply for the city's population. On the other hand, farmers of these area are continuously using untreated solid and liquid waste for the crop production, resulting metal accumulation by food crops and finally in human body. A comprehensive regional survey of trace metals in foods and assessment of their risk to the local population are lacking.

Figure 1-1. Present situation of the study area of three riverine ecosystems around Dhaka City, Bangladesh. (A) Industrial waste burning on agriculture field, (B) river water using as irrigation, (C) industrial waste dumping site and (D) effluents from coal burning power plant.

1.4   The purpose of this thesis

The aim of this study is to identify legacy and contemporary issues impacting trace metal concentration and their distribution to the environment. With best of my knowledge, no detailed study on geochemical fractionation of sediment and soil concerning trace for the study site (or for the area of Dhaka city, Bangladesh) metals has so far been conducted. Therefore, the aim of this research work to determine the distribution, seasonal variation, geochemical fractionation of trace metals in the environmental media and foodstuffs and to assess the contamination from metals around the riverine urban area, Bangladesh.

(i) To investigate the concentrations of six trace metals (Cr, Ni, Cu, As, Cd and Pb) in soil, sediment, water and foodstuffs.

(ii) To see the seasonal variation of trace metals among the environmental samples.

(iii) To assess human health risk of trace metals associated with the exposure from soil and foodstuffs.

1.5 Thesis outline

This thesis is organized into seven chapters. It begins with a general introduction in chapter 1 (this chapter), which introduces the contaminants that were investigated and the purpose of this research. Pertinent literature regarding the sources and movement of trace metals in the environment, geochemical fractionation and risk assessment procedure and the sampling techniques involved in the monitoring of these pollutants are reviewed in chapter 2.

The research carried out and its findings are described in detail in chapters 3–6. Chapters 3 and 4 are devoted to activities and findings of trace metals in the aquatic environment. Specifically, chapter 3 presents a detailed assessment procedure of metals in water and sediment with seasonal variation. An analysis on chemical speciation behavior of trace metals in sediment is presented in chapter 4. Chapters 5 and 6, respectively, present detailed discussion on the metal contaminations in soils of different land uses in Dhaka City. Monitoring of trace metals in the commonly consumed foodstuffs and relation to health risk is presented in chapter 7. A general discussion of the various findings and their implications, as well as conclusions and recommendations for further research are presented in chapter 8.

Supporting information for the various chapters is included in appendix.

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Chapter 2

LITERATURE REVIEW

Literature Review

Abstract

The introductory sections of chapter's 3–7 each contain specific reviews. The issues not covered in those specific reviews but needed to comprehend this thesis are included in this chapter. Essentially, this chapter reviewed the role played by the distribution of trace metals in various environment and the approaches to the monitoring of trace metals, chemical partitioning behavior in soil and sediment, metal transfer from soil to vegetables and health risk assessment. The few examples cited in this review pertain to metal pollution since these are the pollutants of interest in this thesis.

2.1 Summary

Trace metals are ubiquitous in the environment, as a result of both natural and anthropogenic activities. They are stable and cannot be degraded or destroyed, and therefore, tend to accumulate in the environment. In recent years, there has been considerable concern over the extent of contamination of environment with toxic elements and their relationship to public health. Trace metals concentrations in fish and vegetable species are the most important aspect for their toxicity to humans. The accumulation of trace metals in the environment cause a potential health risk due to the transfer in aquatic media, flora and fauna and their subsequent introduction into the food chain.

The disposal of untreated waste may be resulted in the release of trace metals in the environment. The contamination of foods with trace metals may poses threats to its quality and safety. Foods grown in the nearby industrial sites also are contaminated by the relevant trace metals, especially Cd, Cr, As and Pb, which could be a potential health concern to the local residents. Trace metals in sediments and fishes have now been shown to threaten the health of aquatic flora and fauna. Therefore, it is important to control the source of pollution. A long-term risk assessment needs to be carried out on the leach ability and migration potential of the toxic chemicals at the contaminated sites. The potential health risks of trace metal exposure from foods consuming will be considered based on the estimated daily intake (EDI) and the hazard quotients (HQs).

2.2 Sources and movement of metals in the environment

Trace metals are the most common environmental pollutants and their occurrence in water and biota indicates the effect from natural or anthropogenic activities. Trace metals in the environment may originate naturally e.g., the original trace metal contents of rocks and parent materials, processes of soil formation and also produce through human activities. Source identification of trace metals in the environment is a great concern to the world scientist. Once metals originate from the source and then release to the environment. Different metals may produce from different sources and similar source may cause to create more than one trace metal. It has been stated that specific local sources such as discharge from smelters (Cu, Pb, Ni), metal based industries (e.g., Zn, Cr and Cd from electroplating), paint and dye formulators (Cd, Cr, Cu, Pb, Hg, Se and Zn), petroleum refineries (AS, Pb), as well as effluents from chemical manufacturing plants may lead to metal input to the environment (Al-Masri et al., 2002).

Anthropogenic activities such as application of contaminated fertilizers, uncontrolled disposal of plastics and abrasions etc. could be responsible for the higher levels of Cd and Pb than background soils (Rahlenbeck et al., 1999; Itanna, 2002; Manta et al., 2002). Human activities such as industrial and energy production, vehicle exhaust, waste disposal, and coal and fuel combustion etc. are the potential sources of trace metals for agricultural soils (Chen et al., 2005; Lucho-Constantino, et al., 2005).

Trace metal contamination resulted mainly from dumping of waste, although motor vehicle emissions and debris are likely to have contributed to soil contamination with Pb and Zn (Nabulo et al., 2010). Industrial activities and atmospheric emissions are the major contributor of Cd content in the environment. The major sources of Cd in most water bodies include mining through acid mine drainage and battery manufacturing industries. Other probable sources of Cd include leacheates from defused Ni-Cd batteries and Cd plated items (Khan et al., 1992, Stoeppler, 1991).

Among trace metals, Pb is the most interest of research to the scientist due to its harmful activity. Lead is considered as a good indicator of pollution by urban run-off water. The use of leaded gasoline has been mainly responsible for the Pb pollution load during the 20th century in the urban area (Mukai et al., 1994). In Japan from 1980s addition of Pb to gasoline was forbidden but in developing countries still now main source of Pb is considered to be fuel even if other origins are taken into account (Legret and Pagotto, 1999).

The activities of paint and tannery industries and municipal sewage are pervasive processes in the industrial area of Bangladesh, whereas the contribution from pesticides (used for tanning and disinfecting hides) has localized effects (Mohammad et al., 2011). The effluents discharged from the tannery and auxiliary industries and urban sewage system are the main sources of trace metal pollution in the lagoon and canal water systems in the Hazaribagh area of southwestern Dhaka, Bangladesh (Mohiuddin et al., 2011).

The sources of trace metals in the environment are of great interest to the scientist. Source identification of toxic metals is very important for pollution prevention and human health protection. So, it is important to identify the sources of trace metals in the environmental media in the urban area of Bangladesh. This is why more attention is needed to identify the industry or sources for contributing of trace metals in the environment.
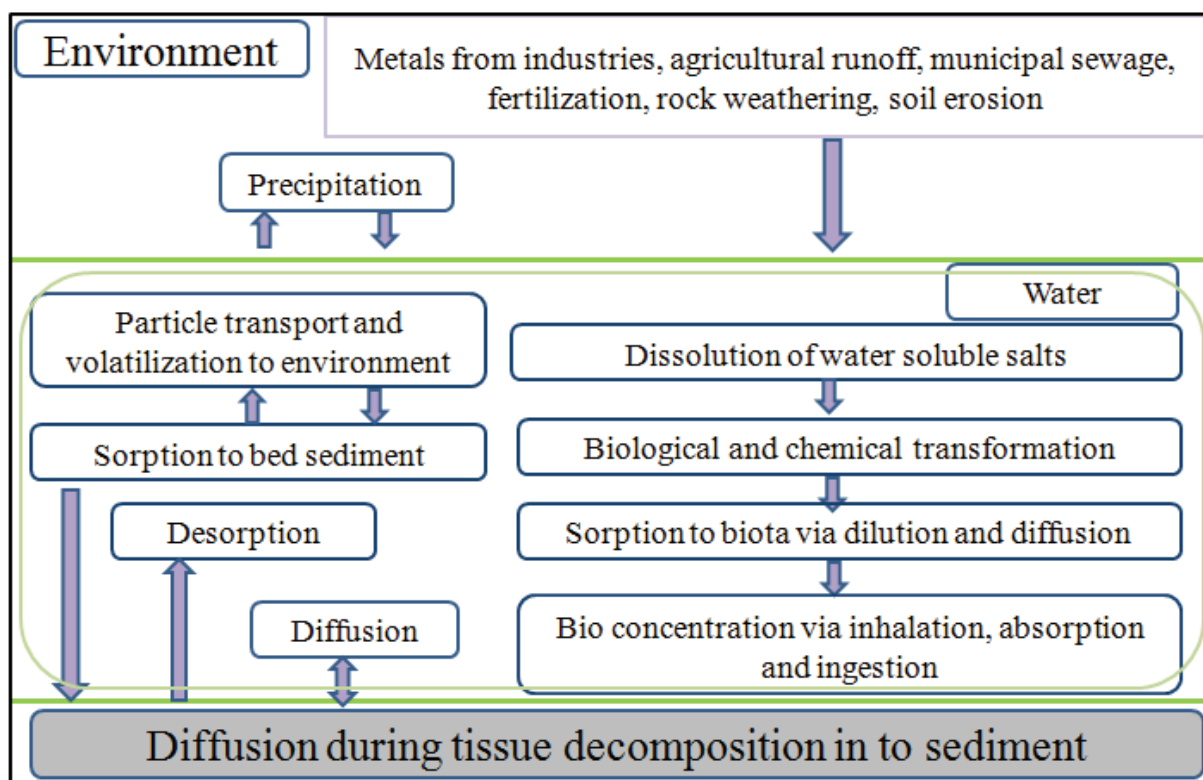
Figure 2-1. Movement of trace metals in the environment.

2.3   Monitoring of trace metals

Monitoring of trace metals in the environmental media (i.e. water, sediment, soil and foodstuffs) is important to know the overall situation of metal pollution in the ecosystem. If any toxic metal released into the environment, it's may accumulate in soil, sediments, water and other biota. The lower aquatic organisms absorb and transfer metals to the higher trophic levels through food chain. Hence, concentrations of trace metals in the organs of fish are

determined primarily by the level of pollution of the water and foods. The contaminants entering into the aquatic ecosystem may not directly damage the organisms and can be deposited into aquatic organisms through bioaccumulation and eventually threaten the human heaths (Lakshmanan et al., 2009).

The accumulation and distribution of trace metals in the environment are increasing at an alarming rate causing deposition and sedimentation in water reservoirs and affecting aquatic organisms as well (Cataldo et al., 2001; Hobbelen et al., 2004; Koukal et al., 2004; Okafor and Opuene, 2007; Mohiuddin et al., 2010; Jain, 2004; Bacon and Davidson, 2008).

Farmers in Bangladesh are continuously using the untreated waste to the field for crop production. In recent years, numbers of agricultural materials such as rice husk, modified cellulosic material, corn cobs, residual lignin, wool, oil mill products, polymerized orange skin, banana husk, pine back, sawdust, coals, etc. have been reported for their removal of toxic metals from aqueous solutions. However, most of these agricultural materials investigated so far have limitations in terms of efficiency and their adsorption capacities for trace metals. Farmers also using the river water as irrigation and river bed sediment for the sources of organic matter. As a result agricultural soils have been contaminated by trace metals. Finally, metals may accumulate in the human body through consumption of foods that are grown on these polluted soils. Therefore, monitoring of these environmental media is needed to know the contamination level in the urban riverine ecosystems in Bangladesh.

2.3.1 Trace metals in surface water

Trace amount of metals are always present in fresh waters from terrigenous sources such as weathering of rocks resulting into geochemical recycling of trace metals in the ecosystems. In the aquatic environment, trace metals may uptake by the organisms through different activities such as bioaccumulation, biomagnification and bioconcentration and cause a long term detrimental effect. The existence of trace metals in the aquatic environment has led to serious concern about their influence on plant and animal life (Sheikh et al., 2007; Zvinowanda et al., 2009).

Islam et al. (2000) emphasized that the largest portion of trace elements such as As, Cr, Ni, Zn etc. dissolved in natural water systems is usually tied up primarily in two forms- as weathered solids of precipitates and adsorbed on the surfaces of particulate material such as organic debris or clay. The behavior of metals in natural water is a function of the substrate sediment composition, the suspended sediment composition and the water chemistry.

Pollutants accumulated in sediments can return to waters in suspended or dissolved form and pose a potential risk to the aquatic biota (Zakir et al., 2006).

Sediment can accumulate many metals that have been released to the body of natural water. The favorable physico-chemical conditions of sediment can remobilize and release the metals to the water column. The behavior of metals in natural water is a function of the substrate sediment composition, suspended sediment composition and the water chemistry (Osmond et al., 1995; Harikumar et al., 2009).

2.3.2 Trace metals in sediment

In recent years, the accumulation of trace metals in aquatic systems is a great concern throughout the world. In the water body toxic metals may accumulate and cause severe impact on the aquatic organisms without any visible sign. In sediment, different types of toxic chemicals have been taken up by the benthic organisms in the process of bioaccumulation, may kill benthic organisms and reduce the food availability for the larger animals like fish. When larger animals feed on these contaminated organisms, the toxins are taken into their bodies, moving up the food chain and increase the concentrations in the process of biomagnification. As a result, fish and shellfish, waterfowl, and freshwater mammals may accumulate hazardous concentrations of toxic chemicals.

Contaminated sediments do not always remain at the bottom of a water body and resuspend due to the effect of dredging. As a result, bottom-dwelling organisms will be directly exposed to toxic contaminants. The knowledge of the chemical forms of the metal in sediments determines their transport and mobility in the aquatic media. The metals can also act as a source of contamination when changes of pH, redox potential, salinity, particulate matter or microbial activity occur in the environment. These changes can increase the mobility and transport of the metals in the aquatic media and make them bioavailable (Rubio and Rauret, 1996).

Many of the sediments in river, lake, and ocean have been contaminated by pollutants. Some of these pollutants are directly discharged by industrial and municipal sewage treatment plants, urban runoff and agricultural activities. Sin et al. (2001) reported that sediment-contained metals ingested by the suspended filter feeder *p. viridis* became bioavailable as sources of metal for mussels. Sediment pollution by trace metals has been regarded as a critical problem in marine environment because of their toxicity and bioaccumulation (Chapman et al., 1998; Islam and Tanaka, 2004; Singh et al., 2005; Todd et al., 2010).

Suspended sediments adsorb pollutants from water, thus, lowering their concentration in the water column. Trace metals are inert in the sediment environment and often considered as the conservative pollutants (Wilcock, 1999; Olivares-Rieumont et al., 2005), although they may be released into the water column in response to certain disturbances, causing potential threat to ecosystems (Agarwal et al., 2005; Chow et al., 2005; Hope, 2006).

Trace metals may be immobilized within the stream sediments and involve in absorption, co precipitation, and complex formation (Okafor and Opuene, 2007; Mohiuddin et al., 2010). Contaminated sediment can decrease the aquatic biodiversity and affect the food chain. The organisms of food chain have been used as biomarkers in assessing level of contaminants in sediment.

2.3.3 Trace metals in soil

Trace metals may increase in the agricultural soil due to the continuous application of chemicals for crop production. From the contaminated soil, trace metals eventually enter to human body through different exposure pathways. This is why metal pollution in agricultural soil has become an important issue both in developed and developing countries (Elsokkary et al., 1995; Nicholson et al., 2003; Micó et al., 2006; Cheng et al., 2007). In Bangladesh, trace metal monitoring in soil is very important because of high risks for humans. There is increasing concern that the lack of suitable land for agriculture is prompting urban farmers to use contaminated land, such as waste disposal sites, burning site, metal workshop site and other commercial area which is exacerbated by rapid population growth, urbanization and industrialization (Nabulo, 2009).

In Bangladesh, the agricultural land is being decreased continuously due to rapid urbanization, industrialization, population growth etc. In the 1980s, there was a dramatic change of agriculture land use to other purposes due to the following reasons: (1) low profit in farming (Jim, 1997), (2) the government posed a positive non-intervention attitude towards agricultural industry without direct subsidization for farmers (Li, 1998) and (3) more importantly, rapid urbanization and industrial development render many rural areas in the new region, leaving many nonconforming land uses (Bryant et al., 1982). Consequently, many farmers or owners of agricultural land prone to changing their land for more profitable uses such as open storage sites, car dismantling workshops and other commercial activities etc.

The non-conforming land uses are potentially dangerous to the surrounding environment and may jeopardize human health (Bryant and Johnston, 1992). This is especially true for the agricultural land which has been used for storing or recycling of

electronic waste containing high levels of trace metals and persistent organic pollutants (POPs) associated with the wastes (BAN and SVTC, 2002; Wong et al., 2007).

Wastewater irrigation is a common practice in most parts of the world due to the shortage of surface water and the presence of nutrients (Charry et al., 2008; Jan et al., 2009). Therefore, long-term application of wastewater results in substantial build-up of trace metals in the receiving soil. Due to repeated application of wastewater as irrigation, the retention capacity of soil decreases which eventually increases the leaching of trace metals into groundwater and plant uptake (Sharma et al., 2008; Jan et al., 2010).

Concentrations of metals in soil, atmospheric deposition, climatic conditions, nature of soil and the degree of maturity of plants are the major factors that affect the uptake and bioaccumulation of metals in crop plants (Khan et al., 2008). Trace metals have been taken by crops and vegetables through absorption from contaminated soils or atmospheric deposition from polluted air. Therefore, trace metal pollution in agricultural soil has serious negative influence on human health (Mueller, 1994; Stalikas et al., 1997; Reimann et al., 2001; Khan et al., 2008). The accumulation of trace metals in agricultural soil is a cause of increasing concern for scientists from all over the world (Facchinelli et al., 2001; Abollino et al., 2002; Huang et al., 2007; Dragovic et al., 2008). The increasing reliance on agrochemicals for higher yields, especially in developing countries, is another important source of trace metals in soils (Li et al., 1997; Wong et al., 2002).

2.3.4 *Trace metals in foods*

In recent decades, food safety is a major concern in the world. The increasing demand of food safety has accelerated research regarding the risk associated with food consumption and contaminated by trace metals (Mansour et al., 2009). Anthropogenic activities, such as mining and industrial processing are the main sources of trace metal pollution in the environment. Moreover, the use of large quantities of agrochemicals such as metal-based pesticides and fertilizers plays an important role in the contamination of foodstuffs by trace metals (Loutfy et al., 2012; Pourang and Noori, 2012).

Trace metal studies on aquatic biota give an idea about the metal concentration in the organisms which could become a more reliable water quality indicator. Marine fish is an important source of high-quality animal protein and long-chain polyunsaturated fatty acids, but also a potential source of toxic metals to higher trophic levels due to fish consumption. One classical example is the Minamata disease in Japan in the 1950s caused by methyl mercury (MeHg) poisoning as a result of marine fish consumption (Wang et al., 2012).

Accumulation of trace metals in fish results primarily from surface contact with water, by breathing, and via food chain. Uptake by these routes depends on the environmental level of trace metals and the habitat of fish. Trace metals do not degrade in water but are generally not found in high concentrations which primarily due to deposition in sediments and uptake by plants and animals (Yi et al., 2008).

High concentration of Pb, Cr and Ni in sediment and fish tissues has been reported especially in areas close to industries. Fish have been reported to be very much sensitive to Pb; its uptake increases with increasing concentration in the environment. Fish living in contaminated sediment showed high Pb concentration (Hewitt and Servos, 2001; Thompson et al., 2000). Zn accumulation in fish results in their mortality, growth retardation and destroys gill epithelium causing hypoxia (Jones et al., 2001). Fish has a tendency to accumulate trace metals from the aquatic environment. If trace metals remain higher concentration in water and sediment, then higher amount may be accumulated in fish. Though there is a variation for trace metals in fish species, but their toxicity is a great concern in respect of human health.

Vegetables contain proteins, vitamins and essential metals and form an important part of the diet as well as act as buffering agents for acidic products formed during digestion process. However, the plants contain a range of concentrations of both essential and toxic elements (Khan et al., 2008). A number of factors such as climate, atmospheric deposition, the concentrations of trace metals in soil, the nature of soil on which vegetables are grown and the degree of maturity of plant affect bioconcentration of trace metals in vegetables (Muchuweti et al., 2006, Lake et al., 1984).

Trace metals uptake capacity varies from species to species even same variety. Now a day, some plant species have been widely used for phytoremediation of trace metals from environment. This is why selection of plant species for trace metal study in the lab scales also an interest to the scientist. Trace metal accumulation in plants depend on plant species, and the efficiency of different plants in absorbing metals is evaluated by either plant uptake or soil-to-plant transfer factors of trace metals (Rattan et al., 2005).

In developing countries, farmers apply different types of chemicals, fertilizers as well as waste as organic matter for crop production which helps to uptake a considerable amount of trace metals. Several studies have indicated that crops and vegetables grown in the metal contaminated soil have higher concentration of trace metals than those grown in uncontaminated soil (Guttormsen et al., 1995; Dowdy and Larson, 1995). As a result, an increased metal uptake by crops and vegetables grown for human consumption is often observed.

2.4   Chemical partitioning of metals in soil and sediment

Over the last few decades, more attention has been given to the determination of species in which a metal is present, since the toxicity, bioavailability, mobility and other properties depend on the chemical association of different components. Sequential extraction of trace metals provides detailed information about the bioavailability and toxicity in the environment and can distinguish the origin of metals such as lithogenic or anthropogenic. It has been stated that sequential extraction schemes are considered as the useful tools for assessing potential metal mobility, bioavailability and toxicity in contaminated sediments and soils (Bryan and Langston, 1992; Davidson et al., 1998). In this sense, in addition to the total concentration of an element in sample, fractionation schemes have been proposed by Tessier et al., 1979, Campbell et al., 1988; Gleyzes et al., 2002 to characterize the chemical forms.

When assessing the possible mobility and environmental impact of trace metals, the analysis of the total metal content is insufficient. It has been stated that bioavailability will vary depending on the nature of metal associations, the mechanisms of metal release from sediments and variation in exposure routes (Chapman et al., 1998; Hickey and Kittrick, 1984; Ajayi and VanLoon, 1989; Jardao and Nickless, 1989; Wallman et al., 1993; Hares, 2000).

Partitioning patterns for trace metals in sediment samples indicated that if metal associates with the oxidizable (organic matter bound) fraction and residual fraction, which allows us to predict the less mobility of metals in sediment and thereby their entry into food chain. On the other hand if metals are more associated with mobilisable fraction (exchangeable and carbonate bound), then metals are considered as more available to aquatic flora and fauna (Chandra Sekhar et al., 2003).

The mobility and toxicity of metals are mainly dependent on metal speciation in the environmental medium. The chemical fractionations of trace metals provide information on metal distribution with different geochemical phases. Higher concentrations of metals in the exchangeable phase would indicate high solubility and bioavailability, meaning that the metals can be more readily taken up by plants grown in soil (Chunling et al., 2011).
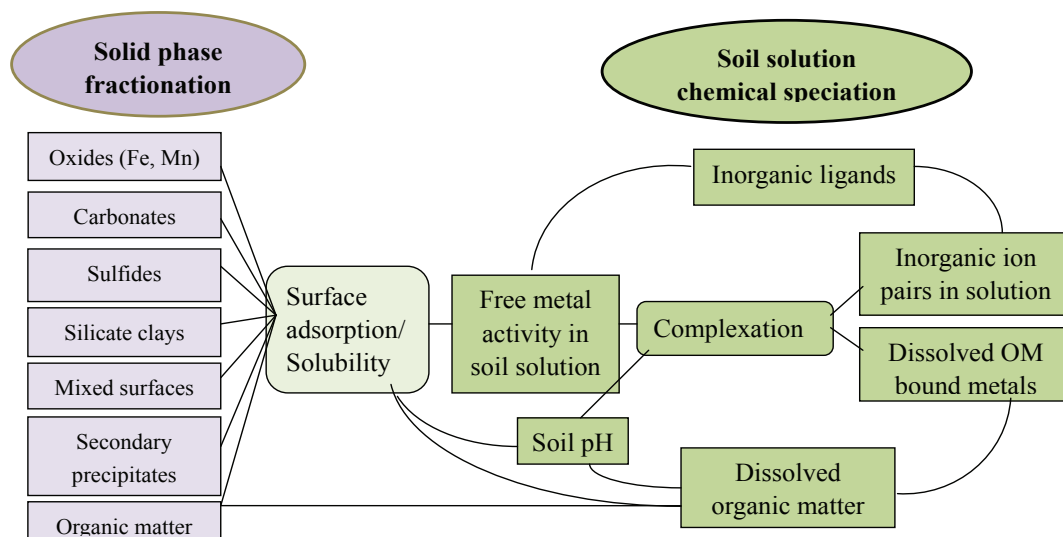
Figure 2-2. Metals pools in solid phase fraction and fractions in soil solution chemical speciation.

Table 2-1. Geochemical fractionation procedure of soil and sediment.

Fraction	Procedure
Fraction 1 (Exchangeable)	Sample extracted at room temperature for 1 h with 7.5 ml 0.05 M NH$_4$OAc with continuous agitation
Fraction 2 (Bound to carbonates)	Residue from fraction 1 extracted with 10 ml 0.17 M acetic acid (pH=7.0) for 5 h with continuous agitation
Fraction 3 (Fe-Mn Oxides)	Residue from fraction 2 extracted with 20 ml hydroxyl ammonium chloride in 25% (v/v) acetic acid (pH=5.0) at 96 $^{\circ}$C with agitation for 5 h.
Fraction 4 (Organic bound)	Residue from fraction 3 extracted with 5 ml 0.02 M HNO$_3$ and 5 ml 3% H$_2$O$_2$, at 85 $^{\circ}$C for 2 h with agitation, followed by the addition of 6 ml H$_2$O$_2$. After cooling, 5 ml of 3.2 M NH$_4$OAc in 20% (v/v) HNO$_3$ agitation for 30 min.
Fraction 5 (Residual)	Residue from fraction 4 extracted with HF/HNO$_3$ (1:1, v/v) mixture and digest.

After each extraction, the samples were centrifuged, liquid-fraction-decanted and 3×10.0 mL of Milli-Q water was added to the residue (sample-centrifuged and water-removed) before proceeding with the next extraction (Stead-Dexter and Ward, 2004).

The use of fractionation procedure permits the determination of how much of the total fraction is available for plants or is accessible to the environment (Quevauviller, 1998). The combination of sequential metal speciation with interpreting of biological data is useful for understanding the link between partitioning and bioavailability. Total metal content for some

trace metals in soil and sediment varies. Therefore, chemical fractionation study is necessary to see the bioavailability for crops and fish.

2.5 Metal transfer from soil to vegetables

The transfer factor (TF) of metals can be used to evaluate the potential capability of plants to transfer metals from soil to edible tissues. Metals with high TF are more easily transferred from soil to the edible parts of plants than ones with low TF. The transfer capability of trace metals from soil to the edible part of vegetable was generally described using the translocation factor (Cui et al., 2004; Greger et al., 2007). Translocation factors (TF) of trace metals were calculated as follows:

$$TF = \frac{\text{Metal concentration in edible part of vegetable}}{\text{Metal concentration in soil where vegetable grown}}$$

Metal transfer from soil to plant is the key component of human exposure through food chain. Metal transfer factor (TF) varied greatly for metals in different vegetables. It has been observed that the uptake of metals by vegetables mainly depended on the bio-availability of metals (Jan et al., 2010; Xue et al., 2011).

2.6 Exposure of metals due to food consumption

Trace metals may enter into the human body via inhalation of dust, consumption of drinking water or ingestion of soil or crops grown on contaminated land (Cambra et al., 1999; Dudka and Miller, 1999). Foods having toxic metals could present a toxic hazard for the consumer which is dependent on the metal concentration in food and amount of food consumed (Hajeb, et al., 2009). For most of the people, the main route of exposure to trace metals is through diet, accounting for > 90 % compared to other ways of exposure such as inhalation and dermal contact (Loutfy et al., 2006; Ryan et al., 1982; Wagner, 1993). It must be noted that although metals can change their chemical form, they cannot be degraded or destroyed. Therefore, the risk assessment of these elements via dietary intake is an important issue (Marti-Cid et al., 2008).

The accumulation of metals in the edible parts of vegetables could have a direct impact on the health of nearby inhabitants, because vegetables produced from fields are mostly consumed locally. Therefore, the concentration of metals in vegetables could be a health concern to the local residents. Trace metals are known to cause deleterious effects on

human health (Davydova, 2005) which can accumulate in human bodies producing toxic, neurotoxic, carcinogenic, mutagenic, or teratogenic illness (Duruibe et al., 2007).

It has been noted that an exposure pathway is not simply an environmental medium (e.g., air, soil, water) or a route of exposure. Rather, an exposure pathway includes all the elements that link a contaminant source to a receptor population. However, for the estimation of metal exposure, variables such as intensity, frequency and duration of the contact with the polluted media are important. For most people, the main route of exposure to toxic elements is through dietary intake (Calderon et al., 2003; Roychowdhury et al., 2003).

Dietary intake of trace metals also poses risk to animal and human health. It has been reported that exposure to two or more pollutants may result in additive and/or interactive effects (Hallenbeck and William, 1993). Excess amounts of trace metals from anthropogenic sources may pollute the environment and ultimately risk to the human health (Brar et al., 2000; Dosumu et al., 2003). A primary concern in urban agriculture is the transfer of trace metals from food chain to humans. Trace metals uptake by plants can cause serious health problems for consumers. Human health exposure to metals occurs as a result of the consumption of contaminated foods and inhalation of contaminated dust particles (Chen et al., 2005).

The daily intakes of trace metals from food consumption for the adult inhabitants have been estimated. The estimated daily intakes (EDIs) of trace metals has been compared with the provisional tolerable daily intakes (PTDIs) suggested by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) or oral reference dose (RfD) to assess the potential health risks. The 'tolerable intake' is widely used to describe 'safe' levels of intake; and can be expressed on either a daily basis (tolerable daily intake) or a weekly basis (tolerable weekly intake). The tolerable intake of trace metals as PTWI (Provisional Tolerable Weekly Intake), are set by the Food and Agriculture Organization/World Health Organization (FAO/WHO) Joint Expert Committee on Food Additives (JECFA). PTWI is the maximum amount of a contaminant to which a person can be exposed per week over a lifetime without an unacceptable risk.

Oral reference doses (RfD) for Ni, Cu, Pb, Cr, As and Cd are 0.02, 0.04, 0.004, 1.5, 0.0003 and 0.001 (mg/kg/day), respectively. The RfD is regarded as an estimate of a daily exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA, 2007). In order to assess the health risk of trace metals in foods, it is essential to estimate the level of exposure by quantifying the routes of exposure of

trace metals to the target organisms. Food chain through foods consumption is one of the most important exposure pathways of trace metals to humans (Muchuweti et al., 2006).

The environmental exposure to trace metals is a well-known risk factor for cancer. Among different pathways, food chain is one of the most important routes for human exposure. In the study area food crops are contaminated with trace metals and consumption of these contaminated food crops can cause risks to human. The association of metal concentrations in foods to that in soils and waters may indicate the extent of contamination by metals and also reveal the potential health risk to consumers.

The health risks associated with trace metals ingested through food consumption will be assessed using the hazard quotients (HQs). The HQ can be defined as the ratio of determined dose of a pollutant to the reference dose (RfD) (mg/kg/day).

$$HQ = \frac{Fir \times C}{RfD \times BW} \times 10^{-3}$$

where, Fir is the food ingestion rate, C is the concentration in foods, BW is the average body weight, and 10^{-3} is the unit conversion factor (Liu et al., 2006; USEPA, 1996, 2000; Wang et al., 2005).

Hazard quotients (HQs) are the ratio between the exposure and the reference doses (RfD), is used to express the risk of non-carcinogenic risks. If HQ is less than 1, there is no obvious risk from the substance, while if HQ is higher than 1, the toxicant may produce an adverse effect. Combined HQ values are sometimes described as 'Hazard Indices', although their application is controversial as their value and significance depend on the number of contaminants involved and the extent to which toxic responses are truly additive (Hough et al., 2004).

Excess consumption of non-essential trace elements such as As and Cd can result in various skin lesions, bone and cardiovascular diseases, renal dysfunction, and various cancers, even at relatively low levels (Calderon, 2000). The consumption of trace metal contaminated food can seriously deplete some essential nutrients in the body that are further responsible for decreasing immunological defenses, intrauterine growth retardation, impaired psycho-social faculties, disabilities associated with malnutrition and high prevalence of upper gastrointestinal cancer rates. It has been found that the high concentrations of metals (Co, Cd, Pb, Mn, Ni and Cu) in vegetables in Van region of Eastern Turkey are related to the high prevalence of upper gastrointestinal (GI) cancer rates (Turkdogan et al., 2003).

In order to assess the health risks, it is necessary to identify the potential of a source to introduce risk agents into the environment, estimate the amount of risk agents that come into contact with the human-environment boundaries, and quantify the health consequence of the exposure.

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Chapter 3

ASSESSMENT OF TRACE METAL CONTAMINATION IN WATER AND SEDIMENT OF SOME RIVERS IN BANGLADESH

Assessment of Trace Metal Contamination in Water and Sediment of Some Rivers in Bangladesh

Abstract

Trace metal contamination is a major problem globally, especially in developing countries. In this study, the levels of trace metals (Cr, Ni, Cu, As, Cd, and Pb) in water and sediment of some peripheral rivers of Dhaka City, Bangladesh, were investigated. Huge amount of municipal wastes, industrial effluents and agricultural runoff from the periphery of Dhaka City notably are dumped to these rivers. Most of the effluents channeled into these rivers are not treated. Sediment and water samples were collected from selected stations along the various rivers in winter and summer seasons and analyzed for the trace metals of concern. Considering the sampling sites, the decreasing order of total metal concentration in water samples were Cr > Cu > As > Ni > Pb > Cd and in sediment were Cr > Pb > Ni > Cu > As > Cd. Total concentrations of Cr, As and Pb in the water samples were higher than WHO guidelines for drinking water quality for some sites. Geoaccumulation index (I_{geo}) revealed high values of Cd for all the stations. The extent of metal pollution in the rivers around Dhaka City implied that the condition is much frightening and probably severely affecting the aquatic ecology of the rivers.

Key words: metal pollution, sediment, river, Bangladesh.

3.1   Introduction

Trace metal contamination of water bodies ranks among the major environmental problems globally, with many issues reported from developing countries in recent times (Wu et al., 2011). The sources of trace metals in these countries are varied, but notably include landfill, mining, tanning, textile and various cottage industries (Bhuiyan et al., 2011). The present study observed the situation of rivers around Dhaka City, the capital of Bangladesh. The city is surrounded by some important rivers notably Turag, Buriganga and Shitalakha. These rivers contribute important socio-economic functions; for instance, they provide water for drinking, washing, fishing, transportation and carrying merchandise across the city. Trace metals can enter the river system through many possible pathways, including disposal of liquid industrial effluents, traffic emissions, brick kilns, terrestrial runoff and leachates carrying chemicals originating from numerous urban, industrial and agricultural activities, as well as atmospheric deposition (Ahmad et al., 2010). Sediments act as adsorptive sink for metals since they can scavenge some elements, thus, much higher metal concentration is found in sediment than in

water column. Sediment, therefore, is an appropriate matrix to monitor the contamination of trace metals in the aquatic environment (Kalantzi et al., 2013). Sediment is regarded as a possible source of contaminants into the water column due to remobilization, desorption, degradation of sorptive substances and redox reactions.

Few studies have been conducted so far especially pointing out on the deterioration of some physicochemical properties of water and sediment of the peripheral rivers of Dhaka City, Bangladesh (Ahmad et al., 2010; Mohiuddin et al., 2011). The present study reports on trace metals in water and sediment in three major rivers of Dhaka City. We conducted an extensive monitoring of trace metals: Cr, Ni, Cu, As, Cd and Pb in water and sediment in different seasons. The study provided an understanding on the extent of contamination of these metals and their spatial and seasonal distribution in aquatic environment of the rivers.

3.2   **Materials and methods**

3.2.1 *Study area and sampling locations*

This study focused on three major rivers Turag, Buriganga and Shitalakha around Dhaka City, Bangladesh (**Figure 3-1**). Sampling was done in winter and summer seasons. Heavy rainfall occurred in summer season and caused higher water flow in river. The metropolitan area of Dhaka is about 815.8 km2 and is located at the center of Bangladesh. The greater Dhaka City is one of the most densely populated cities in the world, home to approximately twelve million people of which less than 25% are served by sewage treatment facility (Ahmad et al., 2010). The basic information's of the study areas are presented in **Table 3-1**

Table 3-1. Basic information of the study area around Dhaka City, Bangladesh.

River	Site ID	Name of the site	Possible pollution source
Turag	T1	Tongi bazar	Cotton mill, brick field, hatcheries, dumping sites for garments waste, pharmaceutical industries observed.
	T2	Ashulia	Textiles, cotton mills, garbage dumping, pharmaceutical industries located to this site.
	T3	Gabtoli bridze	This site is traffic junction, chemical incineration, burning and dumping of industrial effluents, brick fields located to this site.
Buriganga	B1	Basila	The main leather tanning zone, about 270 tanneries on an area of 4 km2, industrial waste dumping, dyeing industries observed
	B2	Kamrangirchar	Urban waste dumping and burning, lead smelting factory, electroplating and city waste sewerage line also connected near this site.
	B3	Buriganga Bridge	It is one of the major industrial location of Dhaka city with units of metals processing, global heavy chemicals Ltd., distillery, paper, textile, glass, electroplating, chemical, plastic, engineering, battery making etc.
Shitalakha	S1	Rupgang	Agriculture field, oil factory, jute mills, cement factory, brick field and ship making factory also located to this sampling site.
	S2	Demra bridze	Waste dispose channel, jute mill, cement factory, glass factory, oil mill observed at this site.
	S3	Shidhirgang	It is downstream site of Kachpur industrial area and located near Shidhirgang power station, waste burning, cement, textiles, spinning, paper and jute mills located to this site.

3.2.2 Sample collection and preparation

Eighteen pairs of water and sediment samples were collected in February-March 2012 (winter) and August-September 2012 (summer). For dissolved metals analyses, water samples were filtered immediately after collection using ADVANTEC® 0.45 μm size sterile syringe filter. In addition, unfiltered samples were collected for total metal analyses. The samples were then transferred into acid cleaned 100 mL polypropylene bottles. The river bed sediment samples (about 200 g) were taken at a depth of 0 to 5 cm using a portable Ekman grab sampler. The lower particle size fraction was homogenized by grinding in an agate mortar, sieved through 106 μm aperture and stored in labeled glass bottles until chemical analyses were carried out.
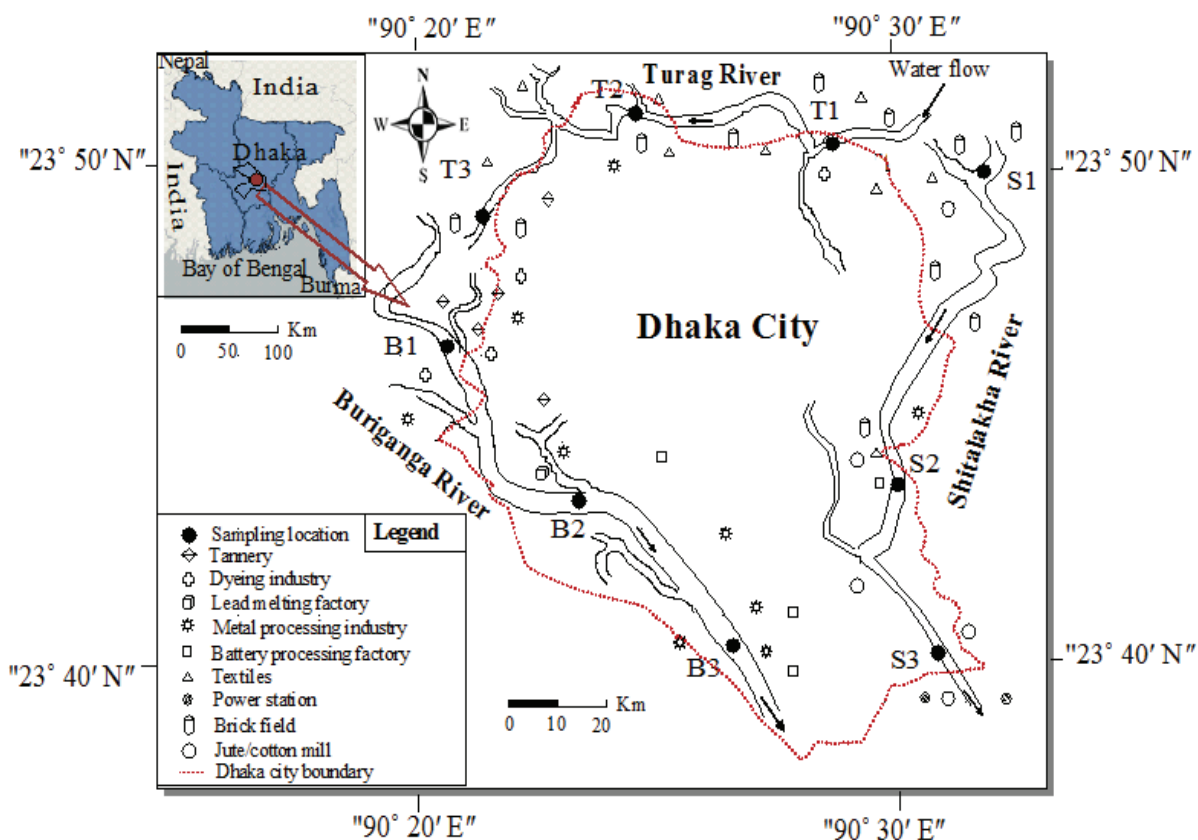
Figure 3-1. Map showing sampling locations in Bangladesh.

3.2.3 Analytical methods for physicochemical parameters

The physicochemical parameters such as pH, EC, %N and %C were measured. The pH of sediments was measured in 1:2.5 sediment to water ratio. The sediment/deionized water mixture was stirred with a clean glass rod and the slurry was allowed to equilibrate for 30 min (Ikem and Adisa, 2011; Ahmed et al., 2012) before taking pH readings. The pH values were recorded using a Horiba U-23 instrument with the calibration of pH 4 and pH 7 standards. For electrical conductivity (EC) determination, 5.0 g of sediment was taken in 50 mL polypropylene tubes. Then, 30 mL of distilled water was added to the tube. The lid was closed properly and was shaken for 5 minutes. After that, EC was measured using an EC meter (Horiba D-52) (Modification after Niwa et al., 2011). Percent N and C of sediment was measured using elemental analyzer (model type: vario EL III Elenemtar, Germany) at Yokohama National University, Japan. For N and C determination, sediment samples were weighed in tin or silver vessels and loaded in the integrated carousel. In a fully automatic process, the transfer of the sample through the ball valve into the combustion tube was performed. Each sample was individually flushed with carrier gas to remove atmospheric nitrogen, resulting in a zero blank sampling process. The catalytic combustion was carried out

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at a permanent temperature of up to 1200°C. The element concentration from the detector signal, and the sample weight on the basis of stored calibration curves were measured. The sediment texture was determined by the hydrometer method (Ikem and Adisa, 2011).

3.2.4. Metal extraction and analysis

Samples were digested in a Berghof-MWS2 model microwave digestion system (Berghof speedwave®, Germany). Digestion reagents that were used included 5 mL 69% HNO_3 (Kanto Chemical Co, Japan) and 2 mL 30% H_2O_2 (Wako Chemical Co, Japan). The weighed samples (20 mL water and 0.2 g sediment) were then placed into a Teflon vessel (DAP-60K type pressure vessels Berghof, Germany) with the digestion reagents. After digestion, samples were transferred into a Teflon beaker and total volume was made up to 25 mL for water samples and 50 mL for sediment samples with MilliQ water (Elix UV5 and MilliQ, Millipore, USA). The digested solution was then filtered using a syringe filter (DISMIC ® - 25HP PTFE, pore size=0.45 μm) from Toyo Roshi Kaisha, Ltd., Japan, and stored in 50 mL polypropylene tubes (Nalgene, New York). For trace metals, samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700 series).

3.2.5 Assessment of metal pollution in sediment

The degree of contamination from the trace metals could be assessed by determining the geoaccumulation index (I_{geo}). The index of geoaccumulation (I_{geo}) has been widely applied to the assessment of soil and sediment contamination (Santos Bermejo et al., 2003). In order to characterize the level of pollution in the sediment, geoaccumulation index (I_{geo}) values were calculated using the equation

$$I_{geo} = \log_2[C_n/1.5B_n] \tag{1}$$

where C_n is the measured concentration of metal n in the sediment and B_n is the geochemical background value of element n in the upper continental crust (UCC) (Rudnick and Gao, 2003; Yu et al., 2011; Rahman and Ishiga, 2012). The factor 1.5 is introduced to minimize the possible variations in the background values which may be attributed to lithogenic effects. Geoaccumulation index (I_{geo}) values were interpreted as: $I_{geo} \leq 0$ - practically uncontaminated; $0 \leq I_{geo} \leq 1$ - uncontaminated to moderately contaminated; $1 \leq I_{geo} \leq 2$ - moderately contaminated; $2 \leq I_{geo} \leq 3$ - moderately to heavily contaminated; $3 \leq I_{geo} \leq 4$ - heavily

contaminated; $4\leq I_{geo} \leq 5$ - heavily to extremely contaminated; and $5 < I_{geo}$ - extremely contaminated.

3.2.6 Statistical analysis

The data were statistically analyzed using the statistical package, SPSS 16.0 (SPSS, USA). A Pearson bivariate correlation was used to evaluate the inter-element relationship in sediment. Other calculations were performed by Microsoft Excel 2010.

3.3 Results and discussion

3.3.1 Concentration of trace metals in water

The physicochemical parameters of water from three peripheral rivers of Dhaka City, Bangladesh are presented in **Table 3-2**. The concentrations of total and dissolved metals are shown in **Figures 3-2**, **3-3** and **Tables A.1.**, **A.2**. Among the trace metals (Cr, Ni, Cu, As, Cd and Pb) analyzed, the total concentration of Cr in water was the highest and Cd was the lowest. The total metal concentration in water followed a decreasing order of site-B1 > site-B2 > site-B3 > site-T3 > site-T2 > site-S3 > site-S2 > site-S1 > site-T1. The highest total Cr concentration was obtained at B1 site (96 µg/L) during winter and (82 µg/L) during summer season (**Table A.1**), presumably as a result of the effects from tannery and dyeing industries of this site. Chromium in water supplies is generally found in the hexavalent form which is highly toxic and in higher concentration to be carcinogenic.

Table 3-2. Physicochemical properties of water during two seasons.

Sites	pH		EC (mS/m)		Temperature (°C)	
	Winter	Summer	Winter	Summer	Winter	Summer
T1	8.2	7.8	63	14	23	31
T2	7.6	7.1	56	14	24	32
T3	7.9	7.6	53	24	24	31
B1	6.5	6.8	57	72	25	32
B2	5.7	6.5	54	13	26	32
B3	6.5	6.9	54	15	25	32
S1	7.4	7.3	65	12	25	30
S2	8.1	7.7	55	26	24	31
S3	7.8	7.5	59	18	24	31
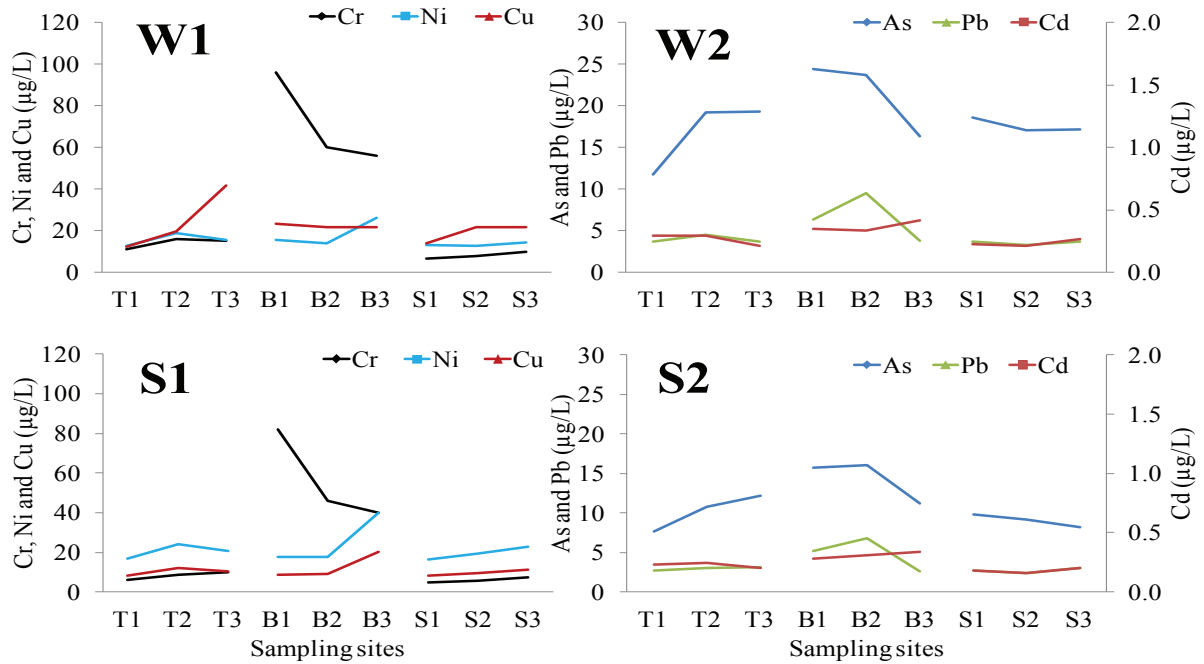
Figure 3-2. Total metal concentration in water during winter (W) and summer (S).
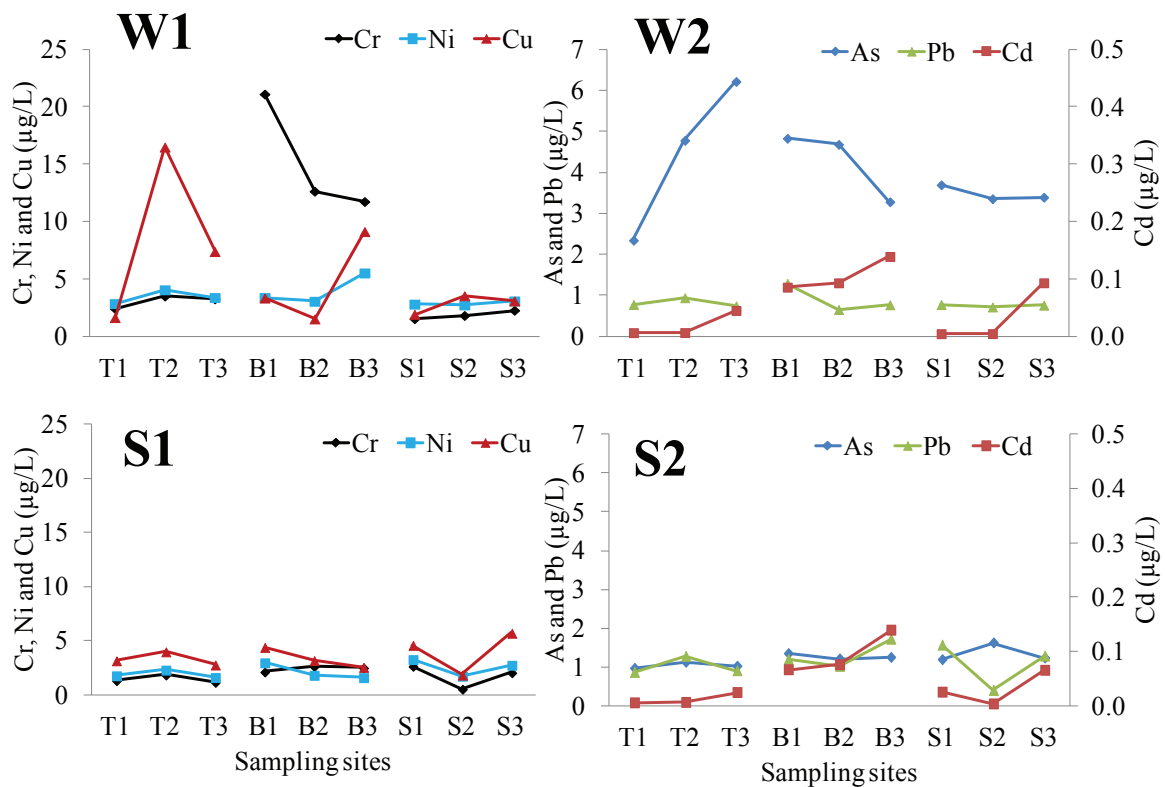
Figure 3-3. Dissolved metal concentration in water during winter (W) and summer (S).

The present study revealed that Cr at all sites in water samples for both seasons were much higher than WHO (5 µg/L) recommended values (**Table 3-3**). High concentrations of nickel (now considered to be a human carcinogen) as both soluble and sparingly soluble compounds may cause changes in muscle, brain, lungs, liver, kidney along with causing cancer (WHO, 2004). Copper in aqueous systems received attention mostly because of its toxic effects on biota. The highest value of total Cu was observed at T3 site (42 µg/L) during winter and B3 site (20 µg/L) during summer, which was close to the densely populated urban area, might be attributed to domestic sewage and runoff from extensively farmed areas (Koukal et al., 2004).

Arsenic forms a variety of inorganic and organic compounds of different toxicity reflecting the physicochemical properties of arsenic at different valence. Among the sampling sites, the highest total As concentration was observed at B1 site (24 µg/L) during winter and (16 µg/L) during summer season, which was higher than the WHO prescribed value for drinking water (**Table 3-3**). However, in river water, higher amount of As comes mostly from sediments (Mitamura et al., 2008) deposited by the river systems from the upland Himalayan catchments as well as the northern part of Bangladesh.

Slightly higher concentrations of total and dissolved Cd were found at B3 site compared to other sites, due to the presence of metal processing, battery factories and paint industries (Caruso and Bishop, 2009). Operations involving the removal of cadmium paints by scraping or blasting might pose a significant increase in winter compared to summer. These kinds of pattern indicate the accumulation of Cd in water during low flow condition of river in winter season. In the study area, total concentration of Pb in water samples ranged from 2.4 to 9.5 µg/L and dissolved concentration of Pb ranged from 0.40 to 1.7 µg/L (**Table A.2**).

Higher concentration of Pb found in the water of Buriganga River might be due to the acidic drainage from the industrial wastes and Pb mineralization. Lead can be carried in water, either dissolved or as waterborne particles. However, few compounds of Pb dissolve readily in water, though most of this Pb is then precipitated and becomes incorporated in the sediments at the base of the watercourse.

A notable increase in pH of Turag and Shitalakha river water, which causes a large amount of metals precipitation, resulted from the formation of their insoluble higher oxides. Similar result for metals in river water was observed by Vicente-Martorell et al. (2009) and Aktar et al. (2010). The lower levels of trace metals during summer might be due to the dilution effect of water. However, seasonal industrial operation along with domestic,

municipal and agricultural wastes might have direct effect on the variations of metal concentrations in water.

Table 3-3. Maximum permitted trace metal concentrations (μg/L) for drinking water quality.

Water quality guidelines	Cr	Ni	Cu	As	Cd	Pb
DWSB[a]	50	100	1000	50	5	50
TRV[b]	11	52	9	150	2.2	2.5
WHO (2004)	5	70	2000	10	3	10

[a] Drinking water standard for Bangladesh proposed through ECR (Department of Environment, Government of the People's Republic of Bangladesh (1997).
[b] TRV (Toxicity Reference Value) for fresh water proposed by USEPA (1999).

3.3.2 Concentration of trace metals in sediment

The physicochemical parameters and textural class of sediments are presented in **Tables 3-4** and **3-5.** Seasonal distribution of trace metals viz. Cr, Ni, Cu, As, Cd, and Pb in sediment samples are presented in **Figure 3-4** and **Table A.3**. The sites generally have pH ranging from 6.3 to 7.4 which was neutral or slightly acidic except at T1 site where pH was 8.7 indicating slightly alkaline condition. The composition of the organic carbon in sediment samples were varied among the sites due to its origin in the aquatic environment. The organic carbon in sediments ranged from 0.18 to 3.3% (**Table 3-4**). The highest percentage of organic carbon might be attributed to the high amount of drainage water at B3 site. According to the United States soil texture classification, the textural analysis revealed that the sediment belonged to the sandy loam, silt loam, silty clay loam, silty clay and clay loam class (**Table 3-5**). Fine sediment textures are important for geochemical carriers which can control metals bioavailability for the aquatic organisms exposing through dissolved metals. A wide range of values for metal concentrations were observed among the sampling sites. Factors such as salinity, geomorphological setup, and land runoff might have played a role in the variation of metals. Among the trace metals, Cr was the highest in concentration and Cd posted the lowest value. The highest concentration of Cr, 2471 and 2039 mg/kg dw, was obtained at B1 site during winter and summer season, respectively (**Figure 3-4**). The main leather tanning zone with about 273 tanneries were situated on the banks of Buriganga River on an area of 4 km^2 of site B1. The chromium enrichment of sediment could have been caused by two reasons: i)

natural: concentration of Cr-bearing minerals; and ii) anthropogenic: industrial activities such as tanneries and textile factories discharging chromates and dichromate used as oxidants.

Table 3-4. Physicochemical properties of sediment during two seasons.

Sites	pH		EC (mS/m)		%N		%C		C/N ratio	
	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.	Win.	Sum.
T1	6.9	8.7	28	40	0.09	0.16	0.18	1.8	2.0	12
T2	6.9	7.2	40	5.4	0.17	0.15	2.8	1.6	17	11
T3	6.9	6.7	30	6.5	0.11	0.13	0.93	1.2	8.4	9.2
B1	6.3	6.5	41	26	0.17	0.23	1.4	1.6	8.5	6.7
B2	6.3	6.9	27	3.3	0.09	0.14	0.74	1.0	8.0	7.3
B3	7.2	6.7	13	24	0.31	0.05	3.3	0.51	11	9.8
S1	6.4	6.9	9.7	6.2	0.09	0.07	0.84	0.59	9.1	8.3
S2	6.5	6.9	17	10	0.11	0.13	0.89	1.1	8.4	8.5
S3	7.4	7.2	39	14	0.09	0.18	0.66	1.6	7.6	9.0

Note: Win. = winter and Sum. = summer

Table 3-5. Textural class of sediments collected from three rivers around Dhaka City, Bangladesh.

Sites	Sediment texture (%)						Type[a]
	Sand		Silt		Clay		
	winter	summer	winter	summer	winter	summer	
T1	17	20	54	43	29	37	Silt loam
T2	16	10	60	64	24	26	Silty clay loam
T3	56	49	28	26	16	25	Sandy loam
B1	71	58	17	25	12	17	Sandy loam
B2	76	67	18	23	6.0	10	Sandy loam
B3	68	66	19	7.0	13	27	Sandy loam
S1	8.0	13	50	54	42	33	Silty clay
S2	16	18	24	27	60	55	Clay loam
S3	6.0	9.0	61	55	33	36	Silty clay loam

[a]According to the United States Department of Agriculture soil classification system.
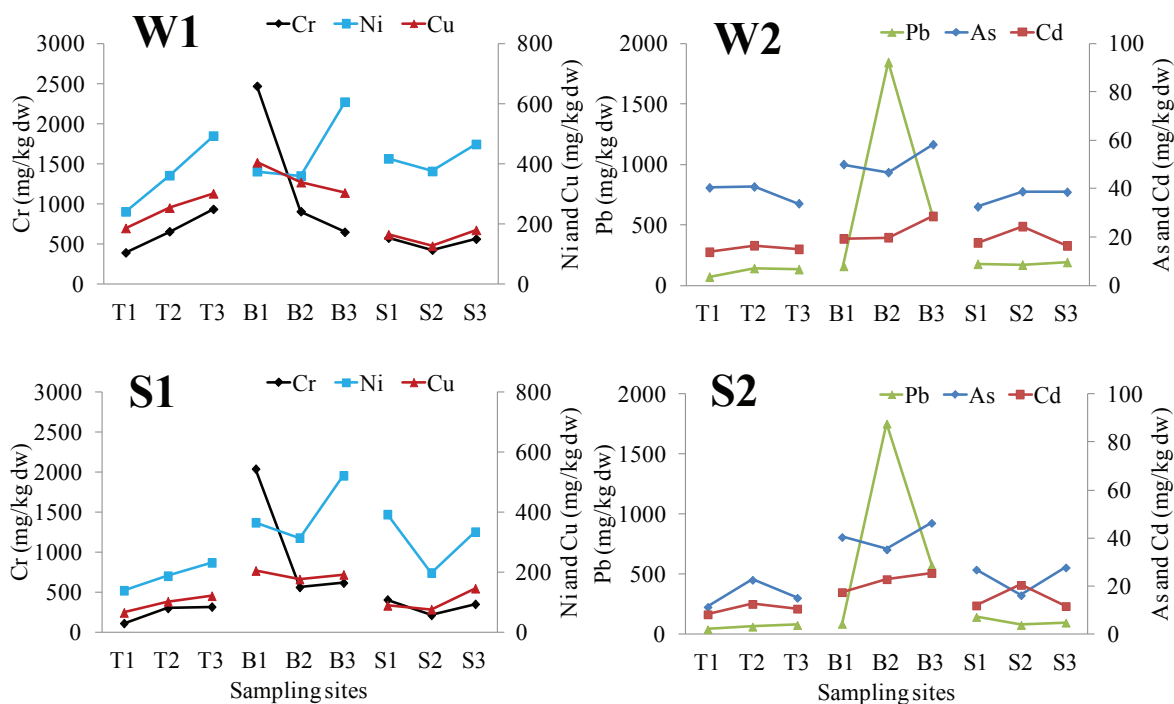
Figure 3-4. Concentration of trace metals in sediment during winter (W) and summer (S).

Hence, the discharging of waste from tanneries was most probably responsible for the high Cr concentration at B1 site. This study has provided the evidence that effluents discharged from the tanneries, dyeing and auxiliary industries and urban sewage system were the main sources of Cr in the river systems of Hazaribagh area of southwestern Dhaka City, Bangladesh (Ahmad et al., 2010). In this study, Ni concentration in sediment showed higher value at downstream site for each river (i.e. T3, B3 and S3). This might be the geochemical trap for Ni bonded in the fine-grained sediment; depositional acceleration of clay mineral and accumulation of Ni adsorbed on clay particles.

Buriganga River sediment samples contained excessive Cu and sampling site B1 recorded the highest Cu content, 404 and 204 mg/kg dw, during winter and summer, respectively (**Table A.3**). The seasonal variation of Cu could be brought about by the organic-Cu compounds formed. Higher level of Cu indicates its higher input in the sites (B1 to B3), which might have originated from urban and industrial wastes. With respect to Cd, B3 site showed the highest value (29 and 26 mg/kg) in both seasons compared with other sites. Higher Cd concentration in sediment of Buriganga River might be related to industrial activity, atmospheric emission, leachates from defused Ni-Cd batteries and Cd plated items (Mohiuddin et al., 2011). Slightly higher Cd levels during winter might be attributed to the variation in water capacity of the river, where water input to the river is generally limited in

winter, resulting in the precipitation of pollutants in the sediment. Arsenic and Cd might reflect the possible formation of complexes with organic matter and thereby slight natural variability of these two metals in surface sediment. There was a large variation observed for Pb in sediment samples in the studied rivers, which might be related to Pb sources and sediment characteristics. The highest concentration of Pb was obtained at B2 site (**Figure 3-4**), attributed to a nearby Pb melting factory. Casting lead and lead product manufacturing are established at the old Dhaka and Keraniganj areas on the southern side of Dhaka City (adjacent to B2 site). In sediment, Pb concentrations in most of the sites were slightly higher in winter compared to summer which indicates that there could be some changes in organic profile due to resuspension/deposition of sediment. Additionally, Pb manifested a little dispersion during both seasons which may be attributed to anthropogenic intrusions.

In order to predict the metal pollution in sediment of the selected rivers, the available data for a comparative analysis with background reference values and other Bangladeshi river sediment values are summarized in **Table 3-6.** It is evident that the average total concentration of all the trace metals in sediment samples exceeded the geochemical background (shale standard and upper continental crust). It is apparent from **Table 3-6** that the concentrations of all metals were very much varied from the average shale values, indicating that these elements did not originate from lithogenic sources. The anthropogenic activities might have contribution to the enrichment of these metals in sediment.

When compared with toxicological reference levels, severe metal pollution was observed for the studied river sediment. The mean concentrations of all the analyzed trace metals were higher than those of the toxicity reference values, lowest effect levels and severe effect level (**Table 3-6**). The mean concentrations of total metals in sediment of the studied rivers were several times higher than those of the sediment of the other Bangladeshi rivers Padma and Jamuna. The results indicate that the levels of trace metals found in the sediment of the rivers might create an adverse effect on the aquatic ecosystem associated with the rivers, especially since it receives urban wastewaters.

Table 3-6. Comparison of metal concentration in sediment with some reference values and some reported values in Bangladeshi river sediment

Metal	Present study [Mean, (Range)] (mg/kg dw)	Sediment quality guideline values (mg/kg dw)					Other Bangladeshi rivers (mg/kg dw)	
		ASV[a]	UCC[b]	TRV[c]	LEL[d]	SEL[d]	Padma[e]	Jamuna[e]
Cr	695 (112-2471)	90	92	26	26	110	97	110
Ni	355 (139-606)	68	47	16	16	75	28	33
Cu	191 (65-405)	45	28	16	16	110	25	28
As	35 (12-58)	13	5	6	6	33	-	-
Cd	17 (8-29)	0.30	0.09	0.6	0.6	10	-	-
Pb	356 (45-1846)	20	17	31	31	250	17	19

[a] ASV- Average shale value proposed by Turekian and Wedepohl (1961)
[b] UCC- Upper continental crust values proposed by Rudnick and Gao (2003)
[c] TRV- Toxicity reference value proposed by USEPA (1999)
[d] LEL- Lowest effect level; SEL- Severe effect level; Ontario Ministry of Environment and Energy through aquatic sediment quality guidelines (Persuad et al., 1993)
[e] Datta and Subramanian (1998)

Statistical analyses were performed in order to elucidate the associations among metals in sediment. Inter-metal interactions may illustrate the sources and pathways of the metals present in the particulate media. Pearson's correlation coefficients for the investigated metals and the physicochemical properties are depicted in **Table 3-7**. A clear pattern of strong association was found among the metal pairs in the sediment samples: Cr-Cu, Cr-As, Ni-Cu, Ni-As, Ni-Cd and As-Cd. Content of Pb was not correlated with any of the studied metals. Higher correlation coefficient between the metals indicated common sources, mutual dependence and identical behavior during their transport.

In the present study, Cr, Ni, Cu, As and Cd metals reflected their similar origins or the processes that controlled their behavior in sediments. Metal and physicochemical associations show pairs Cr/pH and As/pH are correlated with each other, whereas the rest are not significantly correlated (**Table 3-7**). The correlation analysis result indicated that the flocculation or co-precipitation of Cr, Cu and As is influenced by pH (Balachandran et al., 2006). Aprile and Bouvy (2008) have recently shown that limnological processes are natural factors controlling such spatial variations of the heavy metals in sediments. The presence of pH in this correlation is most likely due to its association with Cr, Cu and As (**Table 3-7**). Significant correlation was observed between water and sediment samples of both the seasons for the metals except Pb (**Table 3-8**).

Table 3-7. Pearson correlation coefficient matrix for heavy metals and physicochemical characteristics in sediments (n = 18)

	Cr	Ni	Cu	As	Cd	Pb	pH	EC	%C
Cr	1								
Ni	0.299	1							
Cu	0.712**	0.560*	1						
As	0.542*	0.759**	0.794**	1					
Cd	0.219	0.610**	0.401	0.702**	1				
Pb	0.037	0.168	0.346	0.363	0.456	1			
pH	-0.496*	-0.335	-0.450	-0.480*	-0.448	-0.237	1		
EC	0.411	0.104	0.461	0.288	-0.122	-0.160	0.224	1	
%C	0.081	0.129	0.214	0.161	0.146	-0.110	0.286	0.089	1

** Correlation is significant at 0.01 level (2-tailed).
* Correlation is significant at 0.05 level (2-tailed).

Table 3-8. Correlation of metals between water (total metal) and sediment samples

Metal	water-sediment (winter, n=18)	water-sediment (summer, n=18)
Cr	0.704**	0.576*
Ni	0.949**	0.880**
Cu	0.897**	0.884**
As	0.968**	0.862**
Cd	0.949**	0.892**
Pb	0.453 (0.712**)§	0.401 (0.550*)§

** Correlation is significant at 0.01 level (2-tailed).
* Correlation is significant at 0.05 level (2-tailed).
§ The numbers in parentheses show the correlation coefficients excluding the site B2.

3.3.3 Assessment of sediment contamination

The I_{geo} values showed the following decreasing order: Cd > Pb > Cr > Ni > Cu > As for the studied river (**Figure 3-5**). The highest I_{geo} values obtained for Cd were 6.4 to 7.7 (>5.0) and indicated extreme contamination of sediment in the study area. This might have happened due to higher concentration in sediment and lower geochemical background values resulting to higher I_{geo} values of Cd. The highest values of Cd might be due to contributions from atmospheric emission, leachates from defused batteries and Cd plated items. This is of particular importance as the concentrations of Cd could be detrimental to the majority of benthic organisms. The I_{geo} values for Cr among the locations ranged from 0.9 to 4.0, indicating unpolluted to heavily polluted areas. The range of I_{geo} values for Ni, Cu and As were 1.4 to 3.0, 1.3 to 2.9 and 1.7 to 2.8, respectively, indicating moderate to heavy

contamination. On the other hand, the I_{geo} values for Pb (1.2 to 6.1), indicated moderately to extremely contaminated sediment quality. Chromium and Pb showed outliers for I_{geo} value, because of the extreme concentration of Cr at sampling site B1 (tanning activity) and Pb at site B2 (lead melting activity). The I_{geo} values for Cr and Pb indicated moderately to heavily contaminated sediment, whereas for Ni and Cu was moderately contaminated sediment.
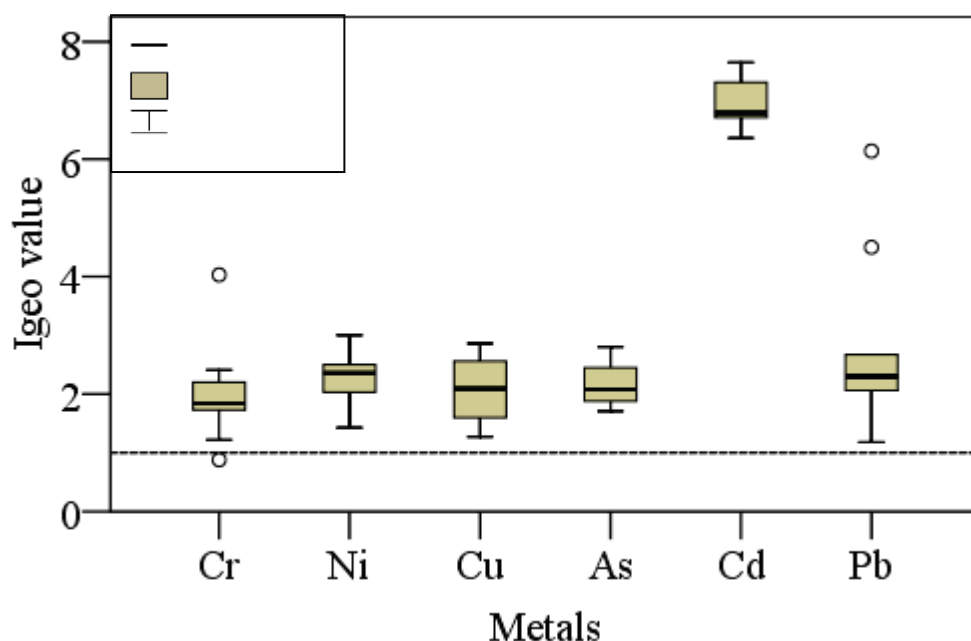
Figure 3-5. Geoaccumulation index (I_{geo}) values of trace metals in sediments of the studied rivers in Bangladesh. Circle symbols represent outlier.

3.4   Conclusions

This study has shown that the sediment of the rivers was heavily polluted with trace metals. Significantly higher levels of metals were observed during winter compared to summer. As some of the selected metals exceeded the safe levels, the water from contaminated sites should not be used without treatment. This study confirmed the seriousness of Cd and Pb levels especially in sediment. Finally, it is concluded that further detailed assessment of these two vital metals are highly recommended for the study area.

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Chapter 4

METAL SPECIATION IN SEDIMENT AND THEIR BIOACCUMULATION IN FISH SPECIES OF THREE URBAN RIVERS IN BANGLADESH

Metal speciation in sediment and their bioaccumulation in fish species of three urban rivers in Bangladesh

Abstract

As a forward step to understand the metal bioaccumulation in fish species, a study of trace metal speciation in sediment was achieved. Trace metals were measured in sediments and three fish species, *Channa punctatus*, *Heteropneustes fossilis* and *Trichogaster fasciata* using inductively coupled plasma mass spectrometer (ICP-MS) after microwave digestion. Abundance of total metals in sediments varied in the decreasing order of Cr > Ni > Pb > Cu > As > Cd. Sequential extraction tests revealed that the studied metals were predominantly associated with the residual fraction, followed by the organically bound phase. The range of metal concentration in fish species were Cr (0.75–4.8), Ni (0.14–3.1), Cu (1.1–7.2), As (0.091–0.53), Cd (0.008–0.13) and Pb (0.052–2.7 mg/kg ww), respectively. The rank of biota-sediment accumulation factors (BSAFs) for fish species were in the descending order of Cu > As > Pb > Ni > Cr > Cd.

Keywords: Chemical speciation, Sediment, Fish, Bioaccumulation, Bangladesh.

4.1   Introduction

Metals and metalloids from natural and anthropogenic sources may enter into aquatic environment and pose serious threat due to their toxicity (Borrego et al., 2002; Olias et al., 2006; Sainz et al., 2004), persistence, bioaccumulation and biomagnification in the food chain (David et al., 2011; Papagiannis et al., 2004; Sankar et al., 2006; Tao et al., 2012). Trace metal pollution in the environment have become a wide concern owing to their ever increasing contamination of water, soil and food in many regions of the world, and particularly in some developing countries like Bangladesh (Ahmad et al., 2010), not only due to the threat to public water supplies, but also they pose ecological and health risk through human consumption of aquatic products (Waqar, 2006; Terra et al., 2008). Therefore, studies on bioaccumulation of pollutants in fish are important in determining the tolerance limits of fish species, effects on fish and biomagnification through food chain (Asuquo et al., 2004). Studies have shown that urban and industrial development contributes with metal

contamination in water environment and aquatic organisms (Tao et al., 2012; Xia et al., 2011). Bangladesh is one of the largest delta regions in the world, formed by the Ganges, Brahmaputra and Meghna and randomly spreading over five countries, namely, Bhutan, Nepal, China, India and Bangladesh (Sharif et al., 1993). Dhaka is the capital of Bangladesh and presents a set of industries that were installed without proper planning and which discharge huge amounts of untreated effluents into the adjacent rivers (Turag, Buriganga and Shitalakha) threating thus the local aquatic ecosystems and the human settlement. In recent decades, the accumulation and contamination of trace metals in these rivers has been paid less attention. Natural and human activities driven the changes and deteriorate the ecosystems of the peripheral rivers of Dhaka City. Besides, these rivers are increasingly being polluted with the city's thousands of industrial units and sewerage lines that continuously discharge huge volumes of toxic wastes (Islam et al., 2006; Ahmad et al., 2010). In addition, a considerable amount of trace metals can be accumulated in the surface sediments of these rivers. In sediment, trace metals are present in a number of chemical forms, and generally exhibit different physical and chemical behaviors in terms of chemical interaction, mobility, biological availability and potential toxicity (Akcay et al., 2003; Singh et al., 2005). During sediment transportation, trace metals undergo various changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena (Abdel-Ghani and Elchaghaby, 2007; Akcay et al., 2003; Dassenakis et al., 1998), which affect their behavior and bioavailability (Nouri et al., 2011). Hence, trace metals are regarded as sensitive indicators for monitoring changes in the aquatic environment. The overall behavior of trace metals in the aquatic environment is strongly influenced by the association of metals with various geochemical phases (Morillo et al., 2004).

It is now widely accepted that the role of sediments as a sink for metal pollutants cannot be fully assessed by measuring the total metal concentration (Chandra Sekhar et al., 2003). Nevertheless, information on total concentration is not sufficient to assess the environmental impact of contaminated sediments (Chandra Sekhar et al., 2003). Therefore, a particular interest on geochemical speciation is needed in assessing the potential environmental impacts and ecotoxicity of trace metals (Sin et al., 2001). Chemical speciation can be defined as the process of identification and quantification of different species, forms or phases of chemicals present in a material (Abdallah, 2012). Metal speciation in sediment is expected to influence metal bioavailability, and thereby metal content in biota, in particular in the soft tissues of fish (Pempkowiase et al., 1999; Yap et al., 2002). To assess the various sediment-bound trace metals into operationally defined fractions, sequential extraction

schemes have been developed by several investigators (Oyeyiola et al., 2011; Pustisek et al., 2001; Rauret et al., 1999; Svete et al., 2001; Sutherland and Tack, 2003; Tessier et al., 1979). Among them, the five stage sequential extraction schemes, developed by Tessier et al. (1979), is extensively used across the world. Sequential extraction techniques would provide the history of metal input, digenetic transformation within the sediments and the reactivity of trace metal species of both natural and anthropogenic origin (Sundaray et al., 2011).

The fresh water fish is important protein source of these countries and fish species selected of this study has commonly consumed by the people. Previous studies on the Buriganga River have focused on the river water chemistry and physicochemical properties in the river water (Ali et al., 2008; Moniruzzaman et al., 2009) and few studies on seasonal and spatial distribution of trace metals (Ahmad et al., 2010; Alam et al., 2003; Mohiuddin et al., 2011). However, no detailed study on geochemical speciation of sediments and bioaccumulation of trace metals in fish species of the peripheral rivers of Dhaka City, Bangladesh has so far been conducted. This research work was conducted to determine the seasonal variation, geochemical fractionation of metals in sediments and to assess the bioaccumulation of metals in three edible fish species.

4.2   Materials and Methods

4.2.1 Study area

Dhaka having 815.8 km^2 metropolitan areas is surrounded by three major rivers "Turag, Buriganga and Shitalakha" (**Figure 3-1**). These rivers are unexpectedly used as a convenient means for disposing of untreated industrial wastes. Dhaka is one of the most densely populated cities in the world with twelve million people of which less than 25% are served by sewage treatment facility (Ahmad et al., 2010; Mohiuddin et al., 2010). The indiscriminate dumping of domestic and industrial wastes, combined with the failure of authorities to enforce existing regulations to protect the ecological health of these rivers, has aggravated the situation to the point where these rivers are dying biologically and hydrologically. Thus, these rivers have been selected for this study and the basic information's of the study areas are presented in **Table 3-1**.

4.2.2 Sample collection and preparation

The sampling was conducted in February-March 2012 (winter) and August-September 2012 (summer), respectively. During winter season no rainfall and the water level in river goes

down and during summer season, the water level in river increase due to heavy rainfall. As a result fish may accumulate different levels of metals from waters of two different seasons. This is why we select two seasons for sampling which gives annual average of metals in fish species. Nine pairs of sediments and fifty four samples of three mostly consumable fish species: spotted snakehead (*Channa punctatus*), stinging catfish (*Heteropneustes fossilis*) and banded gourami (*Trichogaster fasciata*) were collected from three different rivers around Dhaka City, Bangladesh. At each sampling point, composite sediment samples were collected using standard protocol (USEPA, 2001). The river bed sediment samples were taken at a depth of 0 to 5 cm using a portable Ekman grab sampler. Each sediment sample was obtained by mixing sediments randomly collected (3 times) at each sampling point. Fish samples were collected by the help of fishermen. Immediately after collection, fish samples were washed thoroughly with fresh water in order to remove mud or other fouling substances and were put in plastic bag/containers and samples were transported to the Department of Fisheries (DoF), Dhaka University (DU), Bangladesh. After transportation to the laboratory, the fish samples were allowed to reach room temperature and non-edible parts were removed with the help of a steam cleaned stainless steel knife. The edible portion of the fish samples were then washed with distilled water and cut into small pieces (2–3 cm) using the cleaned knife over a clean polyethylene sheet. The samples were then freeze dried to obtain constant weight. The samples were homogenized by grinding in an agate mortar, sieved through 106 μm aperture nylon sieve and stored in labeled glass bottles until chemical analyses. The pre-processed samples were brought to Yokohama National University, Japan, for chemical analysis.

4.2.3 Sample digestion and metal extraction

Samples were digested in a microwave digestion system (Berghof-MWS2, Berghof speedwave®, Germany). Digestion reagents used were 5 mL 69% HNO_3 acid (Kanto Chemical Co, Japan) and 2 mL 30% H_2O_2 (Wako Chemical Co, Japan). The weighed samples (0.3 g of powdered fish) were then placed into the digestion reagent in a Teflon vessel. DAP - 60 K type pressure vessels (Berghof, Germany) which are made entirely of tetrafluoromethoxylene (TFM) were used in this study. Three step-digestion procedures were followed: 1) temperature and power were maintained at 180 ℃ and 85% respectively for 15 min; 2) temperature was kept steady at 190 ℃ for 15 min together with 90% of the power and 3) reduced temperature (100 ℃) and power (40%) were used for 10 min to cool down the Teflon vessels (maximum microwave power is 1000 W when power is 100%). After that, all vessels were kept in cold water to reduce the residual pressure inside the Teflon vessel. After

digestion, the solution was then filtered using DISMIC[®] - 25HP PTFE syringe filter (pore size = 0.45 µm) (Toyo Roshi Kaisha, Ltd., Japan) and stored in 50 mL polypropylene centrifuge tubes (Nalgene, New York). Afterwards, the vessels were cleaned by Milli-Q water and dried with air. Finally, blank digestion with 5 mL 69% HNO_3 following the said digestion procedures were carried out to clean up the digestion vessels (Berghof's product user manual, 2008).

For chemical partitioning of metals, sediment samples were analyzed using Tessier sequential chemical extraction procedure (Tessier et al., 1979). The sequential extraction procedure was divided into five operationally defined chemical fractions: (F1) the exchangeable fraction: readily soluble and exchangeable; (F2) the carbonate bound and specifically adsorbed fraction: carbonate-bound, specifically adsorbed and weak organic and inorganic complexes; (F3) the Fe–Mn oxides fraction: bound to iron and manganese oxides (Fe–Mn oxides); (F4) the organic/sulphide fraction: bound to stable organic and/or sulphide (organic) complexes; and (F5) the residual fraction: held in primary and secondary minerals within their crystal structure. The detailed geochemical fractionation procedure of sediment is presented in **Figure 4-1.**
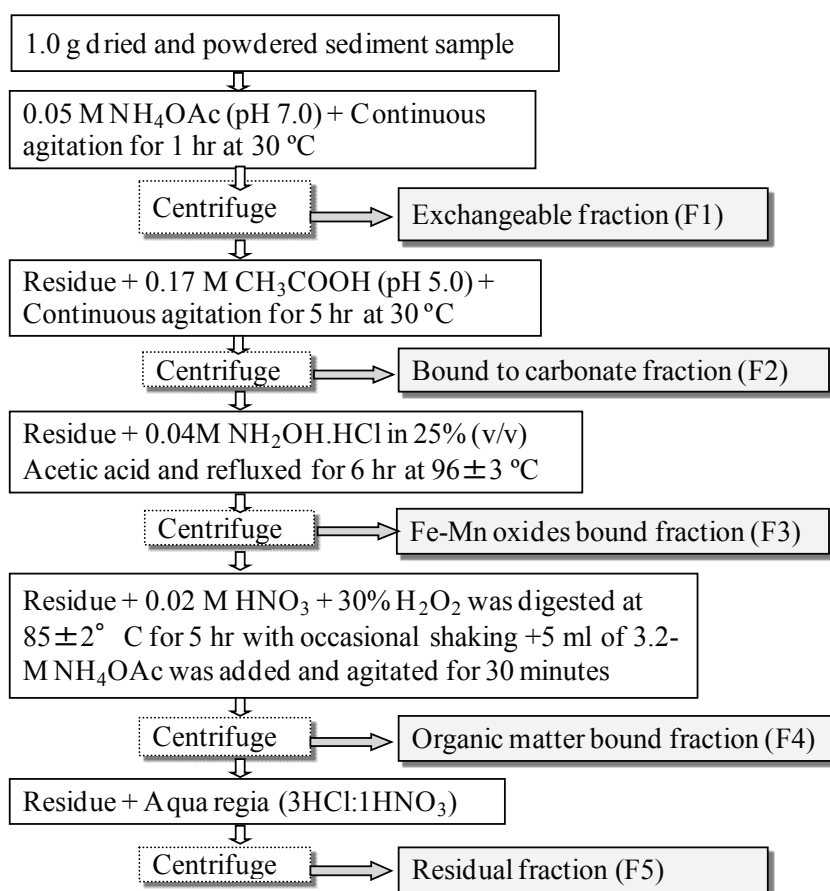
Figure 4-1. Flow chart of the sequential extraction scheme followed in the present study.

4.2.4 Instrumental analysis and quality assurance

For trace metals, samples were analyzed by using inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700 series). Multi-element Standard XSTC-13 (Spex Certi Prep®, USA) solutions was used to prepare calibration curve. The calibration curves with $R^2 >$ 0.999 were accepted for concentration calculation. Before starting the sequence, relative standard deviation (RSD < 5%) was checked by using tuning solution purchased from Agilent Technologies. Internal calibration standard solutions containing 1.0 mg/L of Indium (In), Yttrium (Y), Beryllium (Be), Tellurium (Te), Cobalt (Co) and Thallium (TI) were purchased from Spex CertiPrep®, USA. Multielement solution (Agilent Technologies, USA) 1.0 µg/L was used as tuning solution covering a wide range of masses of elements. All test batches were evaluated using an internal quality approach and validated if they satisfied the defined internal quality controls (IQCs). For each experiment, a run included blank, certified reference materials (CRM) and samples were analyzed in duplicate to eliminate any batch-specific error. The certified reference materials (NMIJ CRM 7303 – Lake Sediment and DORM-2 – dogfish muscle from the National Research Council, Canada) were analyzed to confirm analytical performance and good precision (relative standard deviation bellow 20%) of the applied method and are presented in **Table B.1**.

4.3 Results and discussion

4.3.1 Geochemical speciation of metals in sediment

The mobility and toxicity of metals are mainly dependent on metal speciation in the aquatic environment. The relative distribution of trace metals in different geochemical fractions are presented in **Table 4-1** and **Figure 4-2**. The metals associated with different fractions in sediments followed the descending order of: Cr: Residual > Organic > Fe-Mn oxides > Carbonate > Exchangeable; Ni: Residual > Fe-Mn oxides > Organic > Carbonate > Exchangeable; Cu: Organic > Residual > Carbonate > Fe-Mn oxides > Exchangeable; As: Residual > Fe-Mn oxides > Organic > Carbonate > Exchangeable; Cd: Residual > Exchangeable > Organic > Carbonate > Fe-Mn oxides and Pb: Residual > Organic > Carbonate > Fe-Mn oxides > Exchangeable. Considering the five defined chemical fractions, metals in sediments were higher in winter compared to summer (**Table 4-1**), indicates that there could be some changes in the organic profile due to re-suspension/deposition of

sediment. Slightly higher level of metals during winter might be attributed to the variation in water capacity of the river, where water input to the river is generally limited in winter, resulting in the precipitation of metals in sediment.

Table 4-1. Fraction concentration of metals in sediments [mg/kg dw, (min-max)].

Metals	Exchangeable		Carbonates		Fe-Mn oxides		Organic		Residual	
Season	winter	summer	winter	summer	winter	summer	winter	summer	winter	summer
Cr	10-50	4.4-27	5.0-99	15-40	20-122	10-274	45-997	28-595	256-1195	70-1107
Ni	1.4-4.1	0.82-16	2.8-99	15-63	64-121	27-114	42-117	34-130	110-335	74-236
Cu	2.6-12	1.7-9.9	7.5-25	4.4-27	3.4-12	2.8-23	80-280	16-111	42-135	25-65
As	0.65-1.1	0.32-1.6	2.1-5.5	1.8-3.8	6.1-13	2.8-15	4.7-10	0.74-6.8	20-34	10-30
Cd	3.1-9.3	1.9-6.3	1.9-5.1	1.1-3.7	0.74-2.3	0.50-3.9	1.5-5.2	1.5-4.8	4.9-9.9	2.2-7.6
Pb	5.1-49	3.7-59	20-400	6.0-312	13-120	5.2-346	17-462	11-483	22-815	19-598

Chemical fractionation differentiates metals of natural origin from anthropogenic sources. In general, results of the sequential extraction indicates that the residual fraction dominated the Cr (48–74%), Ni (29–65%), As (40–66%) and Pb (21–44%) during winter and Cr (34–63%), Ni (38–49%), As (43–62%) and Pb (25–42%) during summer season, respectively. This result suggested that Cr, Ni As and Pb had the strongest associations to the crystalline sedimentary components and likely reflected the geological characteristics (Hamilton et al., 1984). Chromium, Ni, As and Pb were the least mobilisable since a considerable proportion of these metals were in the non-mobile fraction, which means they are less available to the aquatic fauna and have less chances of entering into the human food chain (Chandra Sekhar et al., 2003).

According to the partitioning pattern, a considerable proportion of Cd (26% during winter and 25% during summer) was associated with exchangeable fraction (**Figure 4-2**) and can be more available to aquatic life (Zhang et al., 2012). The highest proportion of Cd was bounded for the sum of exchangeable and carbonate fraction (about 40%) reflecting the Cd availability under the high risk category which could easily enter the food chain (Sundaray et al., 2011). The metals like Cd and Pb represent an appreciable portion in the carbonate phase, as these metals have special affinity towards carbonate and may co-precipitate with its minerals. A substantial proportion of Cd (16% and 15%) and Pb (24% and 16% during winter and summer) were found in the carbonate bound fraction (**Figure 4-2**). This result suggested that Cd and Pb can be easily released back into water column, which may cause secondary pollution and at the same time, potential effects on the fish themselves or the organisms that consume them, including top-level receptors, including people (Burger and Gochfeld, 2005;

Dhanakumar et al., 2013). Numerous earlier reports have also considered exchangeable fraction to be the most mobile and bioavailable phase present in the sediments followed by carbonate bound fraction (Ahumada et al., 1999; Howari and Banat, 2001; Tessier et al., 1979). Slight variations were observed in labile fractions (exchangeable and carbonate bound), and lithogenic fractions (Fe-Mn oxides, organic and residual) that could be attributed by numerous factors, such as weathering, mineral transport, anthropogenic inputs, and physicochemical components of sediments (Sundaray et al., 2011). The lower association of Cr (1.2–19% during winter and 1.9–13% during summer) in carbonate fraction in sediments may arise due to the inability of Cr^{3+} to form a precipitate or complex with carbonates (Sundaray et al., 2011).
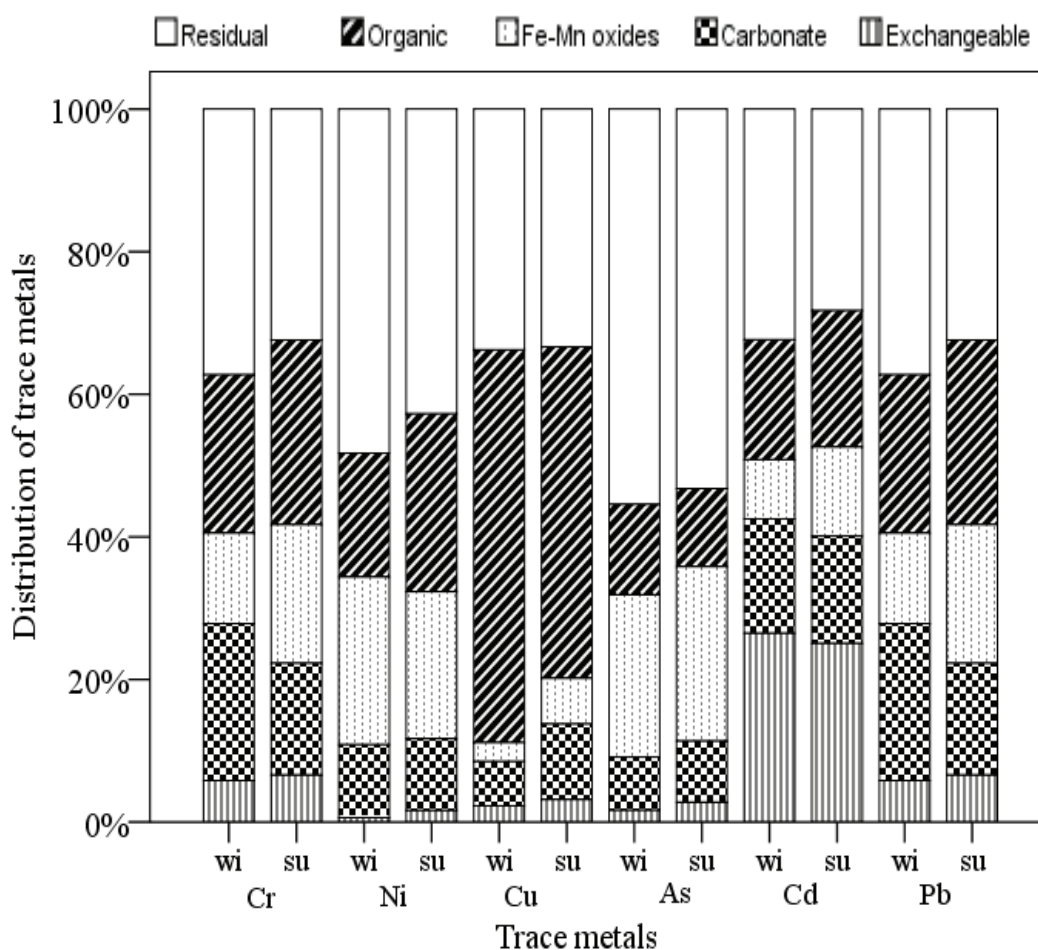
Figure 4-2. Relative distribution of metals in sediment of different chemical fractions.

Fe–Mn oxides and organic matter plays excellent scavengers role for the removal of trace metals from the water column in aquatic environments (Dhanakumar et al., 2013). The reducible fraction contains metals associated with Fe–Mn oxides, which can be mobilized by

changes in the redox potential of the sediments and become bioavailable. Among the non–lithogenic fractions, Fe–Mn oxy-hydroxide is the scavenger for Ni, As and Pb (**Figure 4-2**). This attributes to the adsorption, flocculation and co-precipitation of trace metals with the colloids of Fe and Mn oxy-hydroxide (Rath et al., 2009). Further, organic bound Cr, Cu and Pb seem to be the second dominant fraction among the non lithogeneous. Copper was identified as the highest proportion (45–61% during winter and 24–58% during summer) in the organic fractions. This phenomenon can be explained by the affinity of metals to organic matter, especially humic substances, which are the component of natural organic matter and chemically active in complexing metals (Fytianos and Lourantou, 2004; Jain et al., 2008). Additionally, organic substances are known to exhibit a high degree of preferential selection for divalent ions (Stone and Marsalek, 1996). Copper can be retained by sediment through exchange and specific adsorption but precipitation may also be an important mechanism of retention in polluted sediments. Copper is generally adsorbed to a greater extent than other metals; the high affinity of Cu^{2+} ions for soluble organic ligands may greatly increase their mobility in sediments (McLean and Bledsoe, 1992).

It is recognized that sequential extraction technique enables the prediction of possible metal impact on biota in the aquatic ecosystems. The fractions such as exchangeable and bound to carbonate are considered to be weakly bound. These may equilibrate with aqueous phase thus becoming more rapidly bioavailable and cause environmental toxicity (Karbassi and Shankar, 2005; Kim et al., 1998; Morrison et al., 1996). The metal in sediment of Fe–Mn oxides and the organic matter bound can be mobilized when environmental conditions become increasingly reducing or oxidizing (Karbassi and Shankar, 2005). The metal present in the inert fraction, being of detrital and lattice origin or primary mineral phases, can be regarded as a measure of contribution by natural sources (Salmonas and Forstner, 1980). The variability in the fraction of bioavailable and nonbioavailable of all the studied metals in all sites may be attributed partly to the weathering and transport properties of minerals, anthropogenic inputs and other components of the sediments. However, the contribution from anthropogenic activities is the most important and clearly visible in the river environments.

4.3.2 Metal concentrations in fish species

Although many researchers have presented the elemental contents in various tissues, such as liver, kidneys, gills, gonads and muscles of fish (Ahmed et al., 2009; Moiseenko and Kudryavtseva, 2001; Mzimela et al., 2003), in the present study only fish muscles (edible portion) were evaluated for the elemental concentration since Bangladeshi people do not

habitually consume the other parts. Concentrations of Cr, Ni, Cu, As, Cd and Pb in the muscles of three fish species from three rivers during winter and summer season were presented in **Figure 4-3** and **Table B.2**.
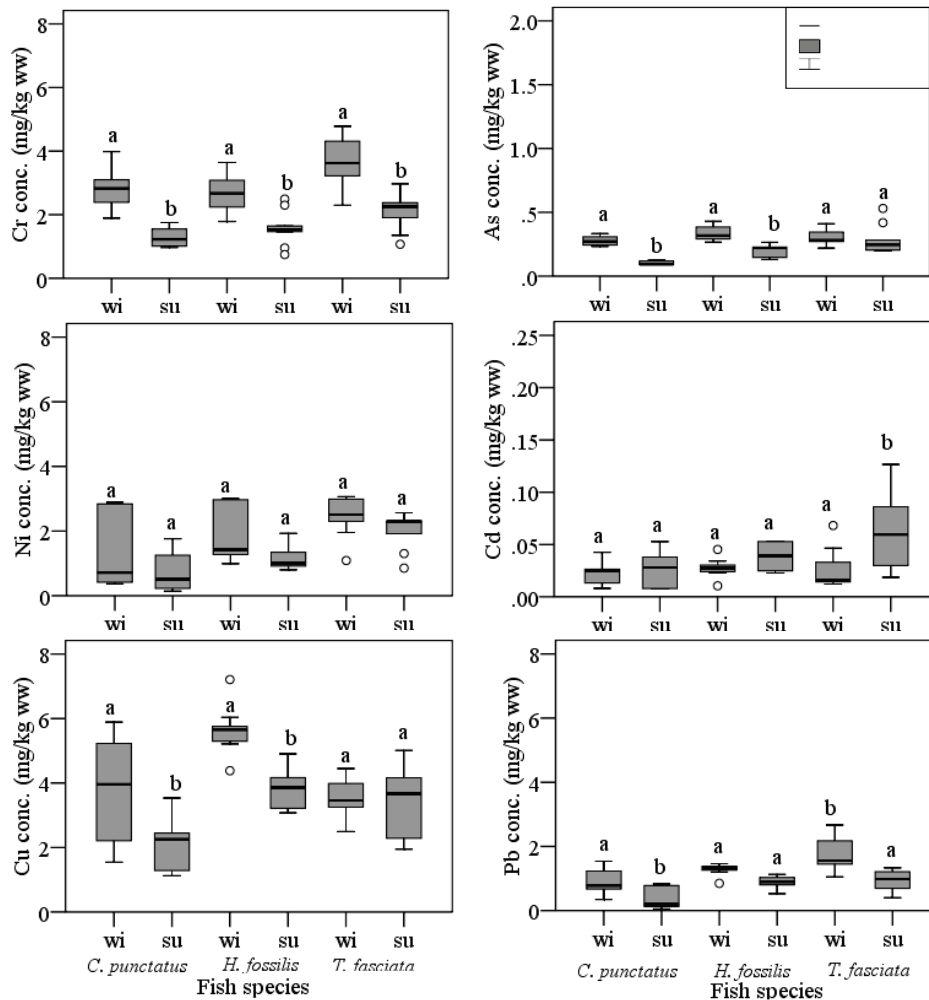
Figure 4-3. Metal concentrations in fish species [mg/kg wet weight (ww)] of two different seasons (winter, wi and summer, su), different letters ("a" and "b") indicate a significant difference ($p < 0.05$) between the seasons of each fish species and circle symbols (o) represent outliers.

From this study, it was revealed that the ranking order of mean concentrations of the trace metals in fish muscles were, Cu (3.74) > Cr (2.35) > Ni (1.59) > Pb (1.02) > As (0.25) > Cd (0.035) (mg/kg ww) respectively. Among the analyzed fish samples, Cr was detected in amount ranging from 0.75 to 4.78; Ni 0.14 to 3.06, Cu 1.12 to 7.21, As 0.091 to 0.53, Cd 0.0077 to 0.13, and Pb 0.052 to 2.67 mg/kg ww. The concentration of metals varied considerably among the fish species. However, as a whole the concentration of studied metals

among the fish species were the following descending order of *T. fasciata > H. fossilis > C. punctatus*. This is because the first two species are sediment ingesting as well as omnivore feeding behaviour and *C. punctatus* is the pelagic fish generally feed from the surface of the water body.

The variation of Cr concentration was observed among the fish species among the studied rivers and seasons. Statistical analyses indicated significant variations of Cr in fish species was observed between two seasons (**Figure 4-3**). During our sampling campaign, we observed that the water level in river during winter season was much lower than summer season. As a result the waste disposal from the industries contributes higher concentration during winter season compared to summer. In the present study, the highest mean concentration of Cr was obtained in *T. fasciata* (4.5 mg/kg ww) during winter season and (2.5 mg/kg ww) during summer season of Buriganga River and the lowest Cr was obtained in *C. punctatus* (2.3 mg/kg ww) during winter and (1.1 mg/kg ww) during summer season (**Table B.2**). Our results showed that the mean concentration of Cr in fish species (2.1–2.8 mg/kg ww) and it was several folds higher than that of fish muscle collected from the Bangshi River, Bangladesh (Rahman et al., 2012), and Calicut fresh water, India (Sankar et al., 2006) indicating a considerable contamination of fishes in these rivers (**Table B.3**). The concentrations of Cr in fish species during winter were higher than summer (**Figure 4-3**). Among the studied rivers, slightly higher concentrations of Cr in fish species was found for Buriganga River, which might be due to the wastewater coming from various industries such as dyeing and tanneries (Mohiuddin et al., 2011; Ahmed et al., 2011a, 2011b). During our sampling campaign, we found more than two hundreds tannery industries and the discharging of untreated waste water to the river. This study has provided the evidence that effluents discharged from the tanneries, dyeing and auxiliary industries and urban sewage system were the main sources of Cr in the river systems of Hazaribagh area of south-western Dhaka City, Bangladesh (Mohiuddin et al., 2011; Ahmad et al., 2010; Rahman et al., 2012). Chromium salts are the most widely used as tanning substances. Only a fraction of the chromium salts are actually consumed during leather processing and most of the salts is discharged as liquid effluent to the nearby river.

Nickel normally occurs at very low levels in the environment and it can cause variety of pulmonary adverse health effects, such as lung inflammation, fibrosis, emphysema and tumors (Forti et al., 2011). In the present investigation, the highest mean concentration of Ni was found in fish species of *T. fasciata* (3.0 mg/kg ww) and *H. fossilis* (3.0 mg/kg ww) and the lowest mean concentration of Ni was obtained in *C. punctatus* (0.18 mg/kg ww) (**Table**

B.2). Copper is an essential part of several enzymes and necessary for the synthesis of hemoglobin (Sivaperumal et al., 2007). Most aquatic organisms have evolved mechanisms to regulate concentrations of Cu in their tissues in the presence of variable concentrations in the ambient water, sediments and food. However, high intake of Cu has been recognized to cause adverse health problem (Gorell et al., 1997). Copper was detected in all examined fish samples and its concentration ranged from 1.1 to 7.2 mg/kg ww, with the highest mean content found in *H. fossilis* (6.0 mg/kg ww) during winter and the lowest mean content was found in *C. punctatus* (1.2 mg/kg) during summer (**Table B.2**).

The concentrations of As in fish species are of great concern with regard to its contamination. Most As is present in food in less harmful (organic) forms. Inorganic arsenic species found in seafood typically account for no more than 1–3% of the total arsenic present (FSA, 2005; Copat et al., 2013) except for the oral As reference dose provided by EPA (3×10^{-4} mg/kg/day) and the tolerable intake for As provided by FAO (0.13 mg/day), as there is no regulatory limit for total arsenic in fish and shellfish, but arsenic exposure is a vital worldwide health concern. Arsenic is widespread in the environment due to both anthropogenic and natural processes. It is a ubiquitous, but potentially a toxic trace element. The toxic effects of As depend on oxidation state and chemical species, among others. Inorganic As is considered carcinogenic and is related mainly to lung, kidney, bladder, and skin disorders (ATSDR, 2003). The mean concentration of As in fish species were observed 0.22 to 0.43 mg/kg ww and 0.091 to 0.53 mg/kg ww during winter and summer season, respectively. Differences in the concentration of As in the fish species were examined and showed that *T. fasciata* had higher than other two species (*P < 0.05*) (**Table B.2**).

Among the studied metals, Cd was detected in the lowest concentration in the fish species. It has been established that Cd occurs in the aquatic organisms and marine environment only in trace concentrations. Nevertheless, it negatively affects several organs: kidney, lung, bones, placenta, brain and the central nervous system (Castro-González and Méndez-Armenta, 2008). Other observed damages include reproductive toxicity, hepatic, hematological and immunological effects (ATSDR, 2008). Several studies have demonstrated that Cd preferentially accumulates in the organs of fish such as the liver and kidney and but not in muscles, where the concentrations are usually very low (Castro-González and Méndez-Armenta, 2008). The highest mean concentration of Cd was found in the fish sample of *T. fasciata* (0.095 mg/kg ww) of Buriganga River and the lowest mean concentration of Cd was found in *C. punctatus* (0.008 mg/kg ww) of Turag River (**Table B.2**). Differences in the concentration of Cd in fish species showed that *T. fasciata* contained significantly higher Cd

than the other two species (**Figure 4-3**). Considering the variation of Cd in fish species, significant differences were observed among the rivers, indicated that fish collected from Buriganga River contained higher Cd than the other two rivers. Higher Cd concentration in fish species of Buriganga River might be related to industrial activity, atmospheric emission, leachates from defused Ni-Cd batteries and Cd plated items (Mohiuddin et al., 2011).

Lead is a non-essential element and well documented that Pb can cause neurotoxicity, nephrotoxicity, and many others adverse health effects (Garcia-Leston et al., 2010). Children are particularly sensitive to Pb with critical effects in the developing nervous system (Castro-González and Méndez-Armenta, 2008). The results of the present study indicated that there was sufficient accumulation of Pb in the muscles of the two sediment harboring fish species (*T. fasciata* and *H. fossilis*). Among individual species, *T. fasciata* (2.5 mg/kg ww) contained the highest Pb concentration during winter, whereas, *C. punctatus* (0.13 mg/kg ww) contained the lowest during summer season. Significant difference was observed for Pb concentration in fish species for two seasons (**Figure 4-3**), which indicates that there could be some changes in organic profile due to resuspension/deposition of the aquatic environment.

The results showed that there was a considerable variation in the concentrations of trace metals from one sample to another. The present study revealed that slightly higher concentration of metals was observed in two fish species (*T. fasciata* and *H. fossilis*). From the literature survey, it was apparent that the fish species of *T. fasciata*, and *H. fossilis* was bottom living and therefore, sediments could be the major sources of trace metals to these fish species. Bottom dwelling fishes are found to exhibit higher concentration of trace metals than pelagic fishes (Gupta et al., 2009). The concentrations of trace metals detected in fishes of this study were compared with the other reported values as an effort to determine the degree of contamination in the study area. In comparison with the concentration of metals in fish and some other studies from Bangladesh and other countries near the industrial area indicated that fishes were contaminated by trace metals (**Table B.3**). The increase of metals in fish species could be mainly due to metal contaminated diet which comes from discharge of effluents into rivers from different industries and other sources in the form of particulates and solutions. However, these fishes might pose contamination due to the continuous consumption from the studied rivers.

Correlation analysis of metal concentrations between fish species and sediment indicated the significant relationship between C. punctatus-sediment and H. fossilis-sediment for Cr, Ni, Cu and Pb. Meanwhile, no relationship was observed (except for Cu) between T. fasciata and sediment (**Table 4-2**). The multivariate Principal Component Analysis (PCA)

was conducted to establish the relationship between the sources and the level of metals in sediments and fish. PCA analysis incorporates the six metal concentration data of all three rivers and explores the possible similar distribution pattern of metals.

Table 4-2. Correlation of metal concentrations between sediments and fish species.

Metals	Sediment-fish species		
	Sediment *C. punctatus*	Sediment *H. fossilis*	Sediment *T. fasciata*
Cr	0.487*	0.339	0.420
Ni	0.560*	0.526*	0.447
Cu	0.433	0.623**	0.634**
As	0.297	0.329	-0.020
Cd	0.074	0.103	0.364
Pb	0.538*	0.289	0.344

* Correlation is significant at 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

In this study, two principal components (PCs) were extracted approximately 89% (PC1: 22%; PC2: 67%) and 98% (PC1: 43%; PC2: 55%) for fish and sediment of the metal variance, respectively (**Figure 4-4**). It was estimated that all metals were strongly associated with PC2 (positive loading) which was mainly exist in the non-bioavailable fractions (> 70%) reflecting the lithogenic origin. Hence, PC2 was supposed to reflect the contribution of natural geological sources of metals into the river. Subsequently, the PCA results showed that PC1 was associated with Cu, Cd and Pb which might represent the anthropogenic sources to the metal pollution.
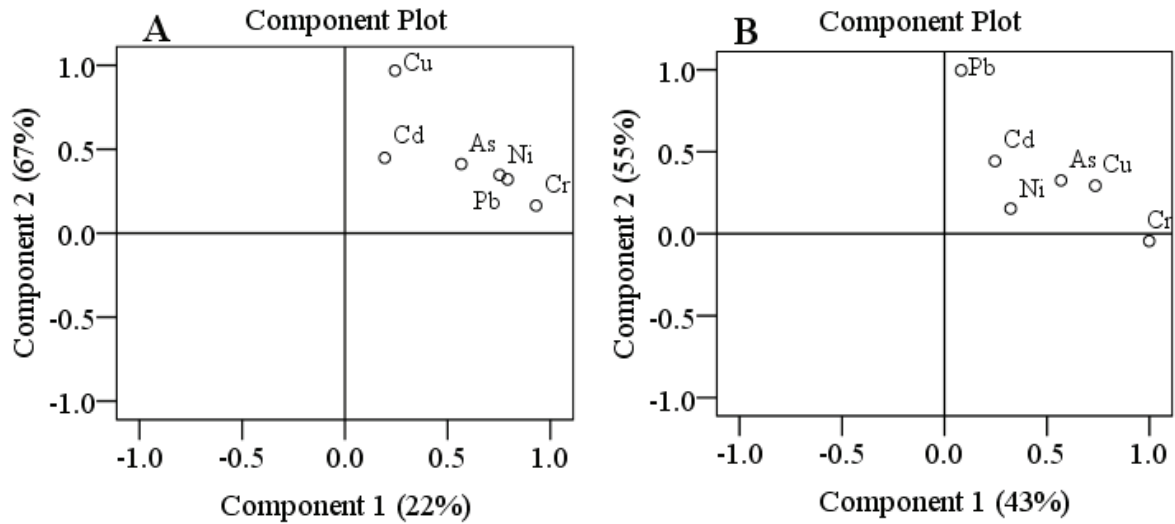
Figure 4-4. The principal component analysis loading plot of the studied metals in (A) fish and (B) sediments from three rivers (Turag, Buriganga and Shitalakha) around Dhaka City, Bangladesh.

4.3.3 Metals bioaccumulation in fish species

The average metal concentrations in fish species and sediments from the studied stations were used for calculating biota-sediment accumulation factor (BSAF). The BSAF is an index of the ability of the fish species to accumulate a particular metal with respect to its concentration in sediment. It was calculated by the following equation (Abdallah and Abdallah, 2008).

$$BSAF = \frac{C_{fish}}{C_{sediment}} \qquad (1)$$

Where, C_{fish} is the metal concentration in fish (mg/kg dw) and $C_{sediment}$ is the metal concentration in sediment (mg/kg dw). The values for BSAFs are given in **Table 4-3** and **Figure 4-5**. The trends of average BSAFs for metals in fish species were in the descending order of Cu > As > Pb > Ni > Cr > Cd. On the basis of calculated BSAF, Cu had the highest while Cd showed the lowest. The BSAF values for Cu varied from 0.020 to 0.136; 0.041 to 0.197 and 0.034 to 0.127 for *C. punctatus*, *H. fossilis* and *T. fasciata*, which was the highest among the selected six metals, suggesting higher rate of accumulation in fish species.

Table 4-3. Biota-sediment accumulation factors (BSAFs) of metals in fish species (two season average).

Sites	T1	T2	T3	B1	B2	B3	S1	S2	S3
C. Punctatus (n=18)									
Cr	0.022	0.016	0.012	0.004	0.009	0.011	0.011	0.018	0.013
Ni	0.006	0.003	0.003	0.019	0.022	0.013	0.003	0.011	0.005
Cu	0.053	0.029	0.027	0.043	0.050	0.059	0.082	0.130	0.061
As	0.023	0.017	0.024	0.014	0.014	0.012	0.019	0.025	0.022
Cd	0.003	0.002	0.003	0.004	0.003	0.003	0.009	0.005	0.005
Pb	0.021	0.007	0.014	0.027	0.002	0.007	0.009	0.012	0.005
H. fossilis (n=18)									
Cr	0.031	0.014	0.013	0.003	0.009	0.007	0.012	0.021	0.014
Ni	0.017	0.015	0.010	0.019	0.022	0.014	0.009	0.016	0.010
Cu	0.138	0.074	0.072	0.070	0.065	0.057	0.113	0.127	0.095
As	0.033	0.021	0.027	0.022	0.024	0.018	0.034	0.033	0.025
Cd	0.007	0.006	0.006	0.004	0.004	0.002	0.008	0.001	0.005
Pb	0.048	0.035	0.030	0.029	0.001	0.005	0.026	0.031	0.022
T. fasciata (n=18)									
Cr	0.045	0.019	0.018	0.005	0.013	0.018	0.014	0.031	0.017
Ni	0.041	0.035	0.025	0.025	0.026	0.016	0.008	0.027	0.014
Cu	0.092	0.057	0.053	0.051	0.050	0.056	0.047	0.095	0.052
As	0.038	0.024	0.066	0.018	0.023	0.020	0.030	0.043	0.027
Cd	0.004	0.003	0.003	0.006	0.007	0.007	0.002	0.002	0.002
Pb	0.070	0.027	0.045	0.034	0.003	0.007	0.016	0.037	0.021

The mean BSAF values for Cr, Ni, Cu, As, Cd and Pb were 0.013, 0.009, 0.059, 0.019, 0.004 and 0.012 for *C. punctatus*; 0.014, 0.015, 0.09, 0.026, 0.005 and 0.025 for *H. fossilis* and 0.020, 0.024, 0.061, 0.032, 0.004 and 0.029 for *T. fasciata* (**Table 4-3**). The BSAFs for Ni, As and Pb in *T. fasciata* were significantly higher than the values obtained for *C. punctatus* and *H. fossilis* (**Figure 4-5**). This can be explained by the sediment ingesting as well as omnivore feeding behavior of *T. fasciata* which may lead to the much greater BSAFs in this study. Therefore, the fish species investigated in this study, *T. fasciata* can be used as a potential bio-indicator for the contamination of trace metals in those riverine environments.
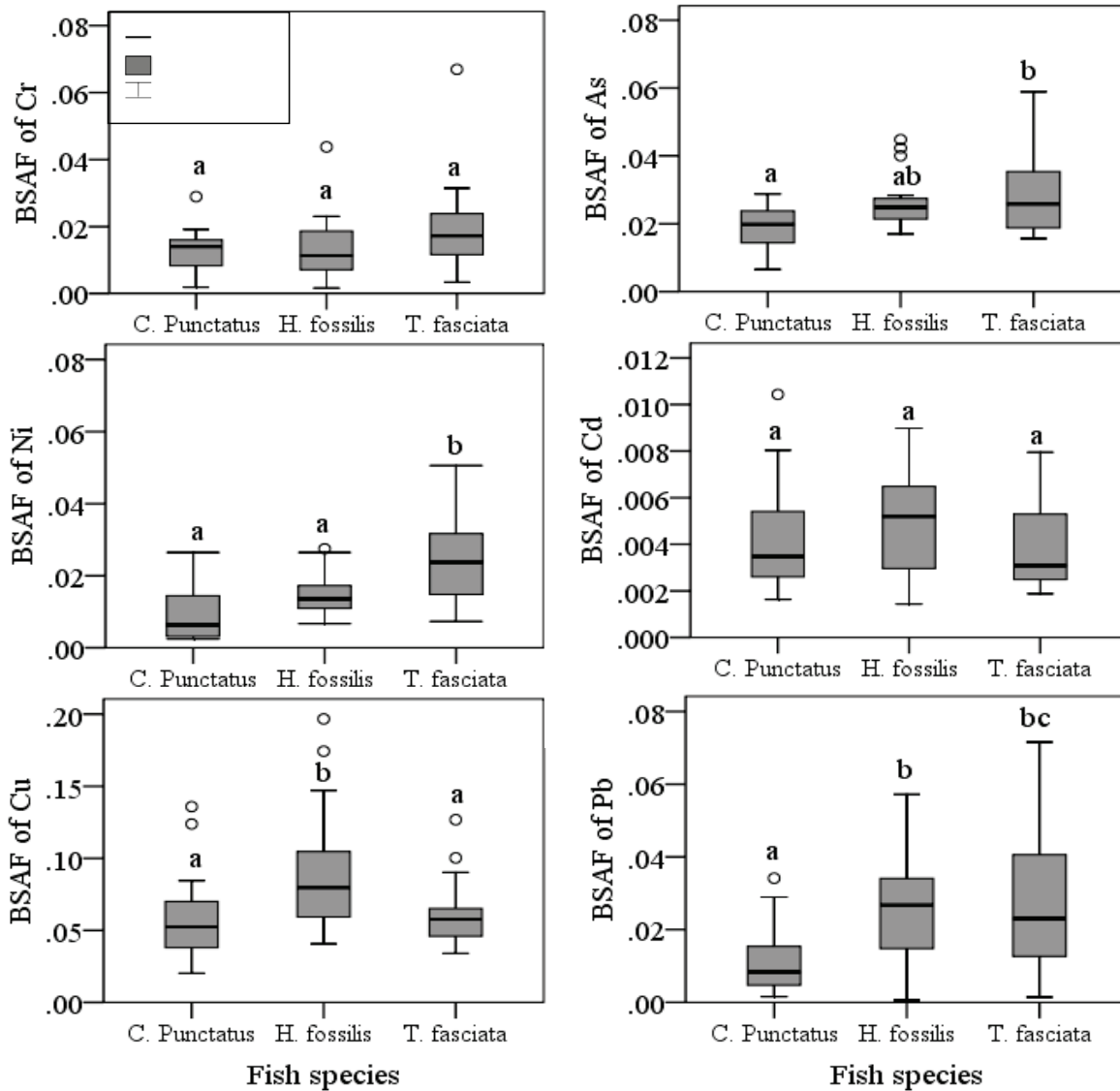
Figure 4-5. Biota sediment accumulation factor (BSAF) of trace metals in fish species. Different letters indicates significant differences ($P < 0.05$) among the fish species and circle indicates the outlier.

The BSAFs of metals in fish species followed the following decreasing order of site T1 > S2 > T3 > S1 > S3 > T2 > B1 > B2 > B3 (**Table 4-3**). The results of BSAFs showed that there was a considerable variation in the bioaccumulation of trace metals from one sample to another. The present study revealed that slightly higher accumulation of metals was observed in two fish species (*T. fasciata* and *H. fossilis*). From the literature survey, it was apparent that the fish species of *T. fasciata* and *H. fossilis* are bottom living and therefore, sediments could be the major sources of trace metals to these fish species. Bottom dwellingfishes are found to exhibit higher concentration of trace metals than pelagfishes (Gupta et al. , 2009). The

bioaccumulations of individual metal among the sampling sites were not similar pattern due to the environment specific phenomenon. It was considered that ingested sediments which found in the digestive tract of fish as an acid ambient, which accelerated the higher amount of metal concentration than it was expected.

4.4   Conclusions

Sequential extraction technique was applied for portioning of selected trace metals in sediments of the studied rivers showing its association with various geochemical forms. Geochemical speciation of trace metals in sediments suggests that Cd, Pb and Cr can pose an adverse impact on aquatic biota and environmental risk due to their higher availability in the exchangeable and carbonate bound fractions. The abundance of metals in chemical fractions was the following decreasing order: residual > organic > Fe-Mn-oxides > carbonate > exchangeable. The concentration of trace metals in *T. fasciata* was slightly higher than *C. punctatus* and *H. fossilis*, which is due to their mode of feeding behavior. Similarly, the calculated values of BSAFs in *T. fasciata* was higher than *C. punctatus* and *H. fossilis*, suggests that *T. fasciata* can be used as potential bio-indicator for metal pollution.

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Chapter 5

TRACE METAL CONCENTRATIONS IN DIFFERENT LAND-USE SOILS IN THE CAPITAL CITY OF BANGLADESH AND HEALTH RISK ASSESSMENT

Trace metal concentrations in different land-use soils in the capital city of Bangladesh and health risk assessment

Abstract

Concentrations of six potentially toxic trace metals: Cr, Ni, Cu, As, Cd, and Pb in twelve different land use type soils were measured for the first time in Bangladesh. Different land use soils, namely, agriculture farm, park area, playground, petrol station, metal workshop, brick field, waste burning sites, disposal sites of household waste, garments waste, electric waste, tannery waste, and construction waste demolishing sites were investigated. The concentrations of Cr, Ni, Cu, As, Pb and Cd in soils were in the range of 2.4–1258, 8.3–1044, 9.7–823, 8.7–277, 1.8–80 and 13–842 (mg/kg), respectively which exceeded the environmental action level for soils. The concentrations of metals were subsequently used to establish hazard quotients (HQs) for the group specific population. The HQs of each metal decreased in the order of As > Cr > Pb > Cd > Ni > Cu. Ingestion was the most vital exposure pathway of studied metals from soils followed by dermal contact and inhalation. The findings of this study revealed that some land-use soils were severely contaminated with toxic metals and suggested to pay more attention regarding the potential health risk to the local inhabitants.

Keywords: Trace metals, land type, exposure pathways, health risk, Bangladesh.

5.1 Introduction

Metal contamination in soil is of great concern due to their long persistence in the environment and toxicity to humans and other organisms (Radha et al., 1997). Naturally, metal can exist in the environment as trace elements in rocks and soils. However, they can be released into the environment as a result of anthropogenic activities (Karakus, 2012). In the urbanized areas, trace metals may originate from various activities such as emissions from vehicular exhaust, application of sewage sludge and wastewater to the arable lands (Thornton, 1991). In the last few decades, the urban environmental pollution has been accelerated due to unplanned urbanization and extensive industrialization. Consequently, urban soils are generally receiving excessive amount of trace metals and other pollutants (Wei and Yang, 2010; Shi et al., 2011; Xia et al., 2011) which lead to the deterioration of the soil biology and

functions, changes in the soil physicochemical properties and create other environmental problems (Papa et al., 2010; Thornton et al., 2008). Recently, lands of Dhaka City have been changed to meet the excessive public demand for the commercial, residential and industrial interests. Depending on the nature, the non-conforming land uses (open storage sites, construction of stations, metal and car workshops, etc.) are potentially hazardous to the surrounding environment and may jeopardize human health (Man et al., 2010). Urbanized cities have been considered as regional sinks for resource consumption and sources of chemical emissions. Because of the proximity to large human populations in the urban areas, soils contaminated with trace metals can pose significant human health risks due to soil ingestion (Luo et al., 2011a; Okorie et al., 2011), inhalation of volatiles and fugitive soil particulates (Laidlaw and Filippelli, 2008), and dermal contact (DEFRA, 2002; Siciliano et al., 2009; Li et al., 2011). The populations those who are involving on certain land use types are the most susceptible to metal exposure from soil (Luo et al., 2012a). Although a number of studies reported on the human health impact due to metal contamination in the urban soils in some regions of the world (Luo et al., 2007; Man et al., 2010, 2013), to our best knowledge, no such study has yet been conducted in Bangladesh and this is the first study reporting the scenario of metal contaminations in urban soils of different land-use types. The objectives of this study are to observe the concentrations of trace metals (Cr, Ni, Cu, As, Cd and Pb) in soils of different land-use types and to assess possible non-carcinogenic and carcinogenic risks through ingestion, dermal contact and inhalation.

5.2   Materials and methods

5.2.1 Study area and sampling

This study was conducted in the urban area of Dhaka city, Bangladesh and targeted twelve different land uses: agriculture farm (AF), park area (PA), playground (PG), petrol station (PS), metal workshop (MW), brick field (BF), household waste disposal site (HW), garments waste disposal site (GW), electric waste disposal site (EW), tannery waste disposal site (TW), construction waste demolishing site (CW) and waste burning site (BS) (**Figure 5-1**). The metropolitan area of Dhaka is about 815.8 km^2 and located at the centre of Bangladesh. Dhaka City is one of the most densely populated cities in the world, home to approximately twelve million people (Islam et al., 2014). Numerous industries (leathers, textiles, metals processing, paper mills, electronic goods, power plant, fertilizers, pharmaceuticals, dyeing, battery

manufacturing, ink manufacturing, Pb-Zn smelting, brick fields, etc.) are situated near the study area (Rahman et al., 2012). The basic information of the study area is presented in **Table C.1.** About 70 composite soil samples were collected during February-March, 2012 and August-September, 2013. Seventy sampling sites were selected depending on the current land uses. At each sampling site, soil sample (up to 10 cm depth) was collected in the form of sub-samples from five different locations. These sub-samples were thoroughly mixed to form a composite sample. Soil samples were air-dried (ISO-11464, 2006) at room temperature for two weeks, then ground and homogenized. The dried samples were crumbled and pulverized with a porcelain mortar and pestle and sieved through 2 mm nylon sieve and stored in airtight clean ziploc bag until chemical analysis. The processed samples were brought to Yokohama National University, Japan, for chemical analysis under the permission of Yokohama Plant Protection Station.
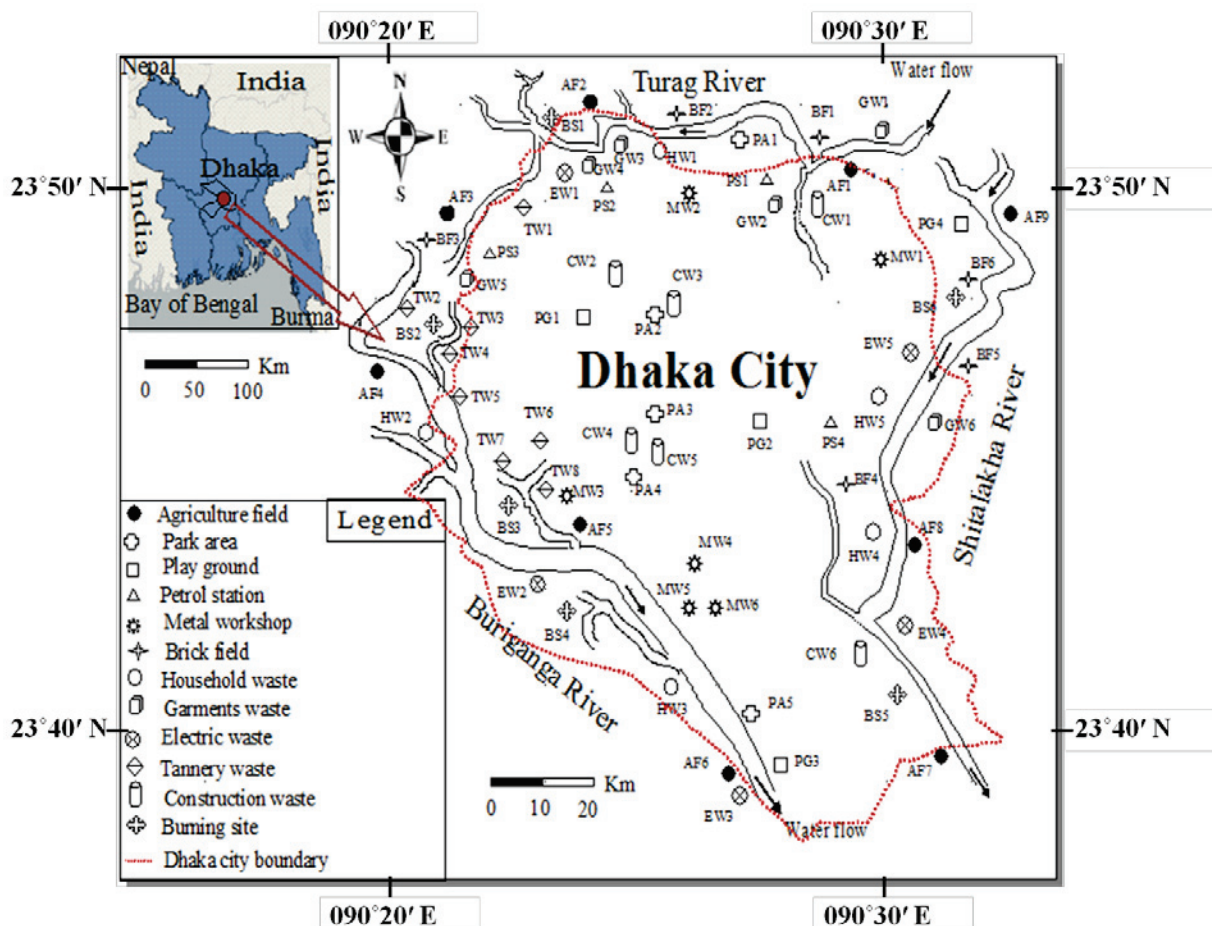
Figure 5-1. Map of the study area in Dhaka City, Bangladesh.

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5.2.2 Sample preparation

All chemicals were analytical grade reagents and Milli-Q (Elix UV5 and MilliQ, Millipore, USA) water was used for solution preparation. The fluon vessel and polypropylene containers were cleaned, soaked in 5% HNO_3 for more than 24 h, then rinsed with Milli-Q water and dried. For total metal analysis, 0.3 g of soil sample was treated with 1.5 mL 69% HNO_3 (Kanto Chemical Co, Japan) and 4.5 mL 35% HCl (Kanto Chemical Co, Japan) in a closed Teflon vessel and was digested in a Microwave Digestion System (Berghof speedwave®, Germany). The digested soil samples were then transferred into a Teflon beaker and total volume was made up to 50 mL with Milli-Q water. The digested solution was then filtered using a syringe filter (DISMIC ® - 25HP PTFE, pore size = 0.45 μm) Toyo Roshi Kaisha, Ltd., Japan and stored in 50 mL polypropylene tubes (Nalgene, New York).

5.2.3 Instrumental analysis and quality control

For trace metals, samples were analyzed using inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700 series). Detailed procedures for quality control are presented in **Chapter 4**.

5.2.4 Health risk assessment

Risk assessment is a multi-step procedure comprising data collection and evaluation, exposure assessment and risk characterization (USEPA, 1989; USDOE, 2011). For performing non-carcinogenic and carcinogenic risk, the mathematical expressions were taken from the US Environmental Protection Agency "Exposure factors handbook" (USEPA, 1997). The method used in this study to calculate the exposure of critical adult inhabitants to Cr, Ni, Cu, As, Cd and Pb in urban soil of different land uses. To our knowledge, there was no study in Bangladesh regarding the exposure frequency and time of metal exposure from soil. So that, we followed some assumptions concerning the exposure frequency and time of metal exposure (based on daily life activities) from different land-use types to the target subjects in Dhaka City (**Table 5-1**).

In this study, six trace metals i.e. Cr, Ni, Cu, As, Cd and Pb were identified as potential hazardous metals to human health. Human exposure to trace metals in the urban soils can occur via three main pathways (De Miguel et al., 2007; Luo et al., 2012b): (I) direct ingestion of substrate particles; (II) inhalation of suspended particulates emitted from soil through the mouth and nose; and (III) dermal absorption of trace metals in particles adhered to exposed skin. Both non-carcinogenic and carcinogenic risks of these exposure routes were

considered. In the step of risk assessment, a specific approach characteristic for human exposure was applied. In this study we considered the following critical population groups those may be affected by trace metals from soils of different land uses in Dhaka City. For instance, the farmers working in the agricultural fields, general people in the park and playground area (involving exercise, play and some entertainments), employee and visitors in the petrol stations, workers in the metal workshops, the daily labors involving in different works concerning the brick fields, household waste, garments waste, electric waste, tannery waste, construction waste dumping sites and waste burning sites.

The carcinogenic risk was calculated for the lifetime exposure, estimated as the incremental probability of an individual developing cancer over a lifetime as a result of total exposure to the potential carcinogen. The non-carcinogenic and carcinogenic risk through each of the three exposure routes were considered and was calculated using Eqs. (1) − (7) adapted from USEPA (1989, 1997) and USDOE (2011).

Calculation of non-carcinogenic risk:

$$HQ_{ing} = \frac{C_{soil} \times IngR \times EF \times ED \times CF}{BW \times AT \times RfD} \tag{1}$$

$$HQ_{dermal} = \frac{C_{soil} \times SA \times AF_{soil} ABS_d \times EF \times ED \times CF}{BW \times AT \times RfD} \tag{2}$$

$$HQ_{inh} = \frac{C_{soil} \times InhR \times EF \times ED}{PEF \times BW \times AT \times RfD} \tag{3}$$

$$HQ = HQ_{ing} + HQ_{dermal} + HQ_{Inh} \tag{4}$$

Carcinogenic risk:

$$CR_{ing} = \frac{C_{soil} \times IngR \times EF \times ED}{BW \times AT} \times CF \times CSF_{ing} \tag{5}$$

$$CR_{dermal} = \frac{C_{soil} \times SA \times AF_{soil} ABS_d \times EF \times ED}{BW \times AT} \times CF \times CSF_{ing} \times ABS_{GI} \tag{6}$$

$$CR_{inh} = \frac{C_{soil} \times ET \times EF \times ED}{PEF \times 24 \times AT} \times IUR \times 10^3 \tag{7}$$

The definitions of symbols, used values of Bangladesh-specific variables and explanation of parameters are shown in **Tables 5-1** and **C.2**. In this study, the non-carcinogenic health risks associated with the metal exposure from soil by the local inhabitants were assessed based on the hazard quotients (HQs) Eq. (1–4). For carcinogens, the dose for As and Pb was multiplied by the corresponding slope factor (**Table C.2**) to produce a level of excess lifetime cancer risk [Eq. (5 and 6)]. Though the effect from interactions between some metals might occur in a synergistic manner (Xu et al., 2011; Luo et al., 2012b), it was assumed that all the metal risks were additive, hence, it is possible to calculate the cumulative non-carcinogenic risk for individual exposure pathway.

The reference dose (*RfD*) (mg/kg/day) is an estimation of maximum permissible risk on human population through daily exposure. The Particle Emission Factor (PEF) relates the concentration of a chemical constituent in soil to the concentration in dust particles in air (USEPA, 1996, 2001) which has been considered for two aspects-presence of vegetative cover (AF, PA and PG) or absence of vegetative cover (PS, MW, BF, HW, GW, EW, TW, CW and BS). If the *HQ* is equal to or higher than 1, there is a potential health risk, and related interventions and protective measurements should be taken.

Table 5-1. Values of the variables for the estimation of human exposure of trace metals from soils of different land use types in the urban area of Dhaka City, Bangladesh.

Variables	Value	References
IngR (mg/d): Soil ingestion rate	100	USDOE, 2011; USEPA, 1997
EF (d/yr): Exposure frequency	180, 200, 100, 200, 200, 125, 250, 100, 24, 200, 24 and 24 for AF, PA, PG, PS, MW, BF, HW, GW, EW, TW, CW and BS, respectively	This study
ED (yr): Exposure duration	30	USDOE, 2011
BW (kg): Average body weight	60	FAO, 2006
ATnc (d): Averaging time for non-carcinogenic effects	ED × 365	USDOE, 2011
ATca (d): Averaging time for carcinogenic effects	LT × 365	USDOE, 2011; USEPA, 1997
LT (yr): Lifetime	70	WHO, 2014
ET (h/d): Exposure time	6, 1, 2, 6, 6, 6, 3, 3, 3, 6, 3 and 3 for AF, PA, PG, PS, MW, BF, HW, GW, EW, TW, CW and BS, respectively	This study
CF (kg/mg): Conversion factor	1×10^{-6}	Man et al., 2010, 2013
SA (cm^2): Skin surface that are available for exposure	3300	Man et al., 2010
AF (mg/cm^2): Soil to skin adherence factor	0.07	USDOE, 2011
ABS_d (unitless): Dermal absorption factor	0.001	USEPA, 2011
InhR (m^3/d): Inhalation rate	20	USEPA, 1997
PEF (m^3/kg): Particle emission factor	1.36×10^9 (presence of vegetative cover), 6.8×10^8 (absence of vegetative cover)	USEPA, 2001

5.2.5 Statistical analysis

The data were statistically analyzed using the statistical package, SPSS 16.0 (SPSS, USA). The means and standard errors of the metal concentrations in soils were calculated. Multivariate Post Hoc Tukey tests were employed to examine the statistical significance ($p < 0.05$) of the differences among mean concentrations of trace metals among sites.

5.3 Results and discussion

5.3.1 Metal contamination in soil

The concentration of six trace metals viz. Cr, Ni, Cu, As, Cd and Pb in soil samples of different land-use types are presented in **Figure 5-2** and **Table C.3**. The mean concentrations

of trace metals in soil were in the following descending order of Cu (267) > Cr (239) > Ni (206) > Pb (195) > As (58) > Cd (16) (mg/kg). The levels of trace metals varied among the sampling sites of different land-use types and followed the descending order of TW > MW > EW > AF > GW > BS > CW > BF > HW > GPS > PG > PA. Metal concentrations were found statistically significantly different ($p < 0.05$) among the studied sites (**Table C.3**). The highest mean concentration of Cr was obtained at the tannery waste disposal site (1112 mg/kg), which can be due to the waste from chromate smelters (McMartin et al., 1999; Krishna and Govil, 2007; Srinivasa et al., 2010). The elevated mean concentrations of Ni were observed at MW and EW site that can be attributed to the emission from metal smelters. Such extremely high levels of Ni in soils can be found in metal industries and waste disposal sites, which result from localized additions or accidental spillages of highly concentrated materials that contain Ni (Govil et al., 1998; Krishna and Govil, 2007). The elevated concentrations of Cu was observed in soil from most of the waste disposal sites which can be due to the emission of Cu from the uncontrolled industrial and waste burning activities (Kashem and Singh, 1999; Srinivasa et al., 2010; Luo et al., 2011b). Among the sites, TW, BF, BS and AF sites showed a considerable level of As. Interestingly, TW site showed the highest As concentration (112 mg/kg). In general, huge amount of ground water containing As (Neumann et al., 2010; Hug et al., 2011) are being used for tanning in relation to some chemicals especially arsenic sulfide (Asaduzzaman et al., 2002; Bhuiyan et al., 2011). Moreover, emission and waste from brick fields and incineration activities might contribute the high concentration of As (Olawoyin et al., 2012). Arsenic in agricultural soils can be derived from both natural and anthropogenic sources, especially use of ground water for irrigation (Neumann et al., 2011), uncontrolled application of As enriched fertilizers and pesticides (Renner, 2004). The elevated mean concentration of Cd was obtained from the EW, MW, TW and BF sites that can be attributed due to the metal processing, battery manufacturing and smelting industries. Severe Cd pollution has been reported from areas surrounding smelters in many countries (Martley et al., 2004; Rawlins et al., 2006). MW, EW and BS sites showed the elevated concentrations of Pb which can be due to the emission of Pb contaminated waste from these sites (Srinivasa et al., 2010; Luo et al., 2011b). During our sampling, we observed leachates from defused Ni-Cd batteries, Cd plated items, casting lead and lead products manufacturing at the sampling sites. From the data, it was observed that some trace metals showed higher standard deviation, and such high deviation may be indicative of the lack of uniformity of the elemental distribution among the sites. This was probably due to various land use activities and disturbances such as digging, excavation, and construction, as well as

other natural processes such as weathering and erosion, which could alter stabilization of the soil environment (Amuno, 2013).
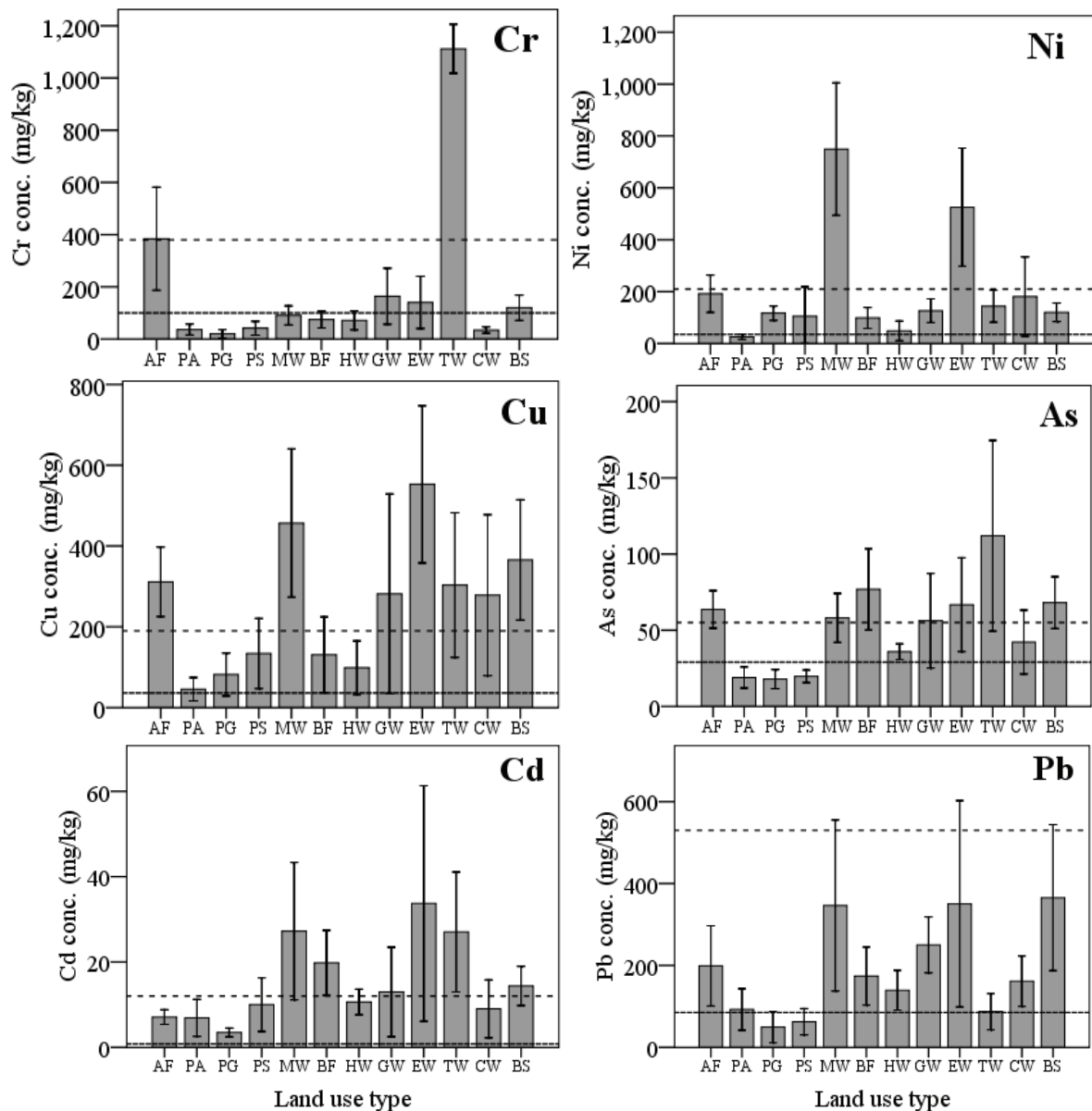
Figure 5-2. Bar chart of trace metal concentrations and their respective Dutch soil quality value in 12 different types of soil. Error bar represents ±SE. (Horizontal dot lines indicated Dutch soil quality standard (Target and Intervention value).

In the present study, we used some international guidelines for trace metals in soil to understand the current situation of metal contamination, since there was no locally-derived environmental standard for trace metals contamination in soil of Bangladesh. Hence, soil quality guidelines from the other countries with protection of ecological receptors were used

to compare with the trace metal levels obtained from this study. The following guidelines were applied: The New Dutch List (VROM, 2000), Canadian Environmental Quality Guidelines (CCME, 2003), China Environmental Quality Standard (SEPA, 1995), Australian Guideline on the Investigation Levels for Soil (NEPC, 1999; DEP, 2003) and Sweden Soil Remediation Goals (SEPA, 2002). The mean concentrations of Ni, Cu, As and Cd in soil from the twelve different land-use types were higher than the aforementioned recommended guideline values (**Table C.3**). The site specific concentrations of the studied metals mostly exceeded the Dutch soil quality target and intervention values (**Figure 5-2**). The functional properties of these soils such as nutrients and contaminants storage, transformation and biomass production, etc. may be seriously affected due to continuous crop production, which could potentially cause adverse effect on humans, plants and animals (VROM, 2000; Man et al., 2010). The present study mainly used the Dutch soil quality standard (VROM, 2000) and regarded as the most comprehensive guideline considering all possible exposure pathways for protecting humans, plants and animals. If any metal concentration in soil is below its respective Dutch Target Value, the soil is considered clean. If the concentration level lies between the target and intervention values, the soil is regarded as slight to moderately contaminated. In contrast, if the value is above the Dutch Intervention Value, the soil is considered detrimental to humans, plants and animals.

5.3.2 Health risk assessment

Trace metals in the contaminated soils might have a serious impact on human health (Okorie et al., 2011). In urban areas, soils of playground, park, residential, industrial areas, brick fields and waste burning sites are considered as the significant exposure media of trace metals through ingestion, dermal contact and inhalation (Mielke et al., 1999; Luo et al., 2011a; Bright et al., 2006; De Miguel et al., 2007; Zheng et al., 2010). According to the risk assessment approach, both the non-carcinogenic and carcinogenic risks of metals through three exposure pathways in urban soils were characterized in this study.

5.3.2.1 Non-carcinogenic risk

The Hazard quotients (*HQs*) of individual metal from different land uses are presented in **Table C.4** and **Figure 5-3**. The *HQs* for the studied metals through soil ingestion were higher than other two exposure pathways indicting the target population of the study area were mostly exposed through ingestion. Similar trends have been reported for urban soils around industrial clusters in Ghaziabad, India (Chabukdhara and Nema, 2013). Among the land uses,

the higher *HQ* values were observed for AF, MW and TW in each of the exposure pathways, implying a potential health risk to the workers and inhabitants living close to these sites. The HQs of each metal were decreased in the order of As > Cr > Pb > Cd > Ni > Cu. Metal specific *HQ* values were less than 1 indicating the intake of single metal through different pathways of soil does not pose a considerable non-carcinogenic risk to the exposed people (**Figure 5-3**). However, current assessment is not taking dietary exposure into account. Exposure from food items harvested in contaminated agricultural field should be considered in the future assessment.
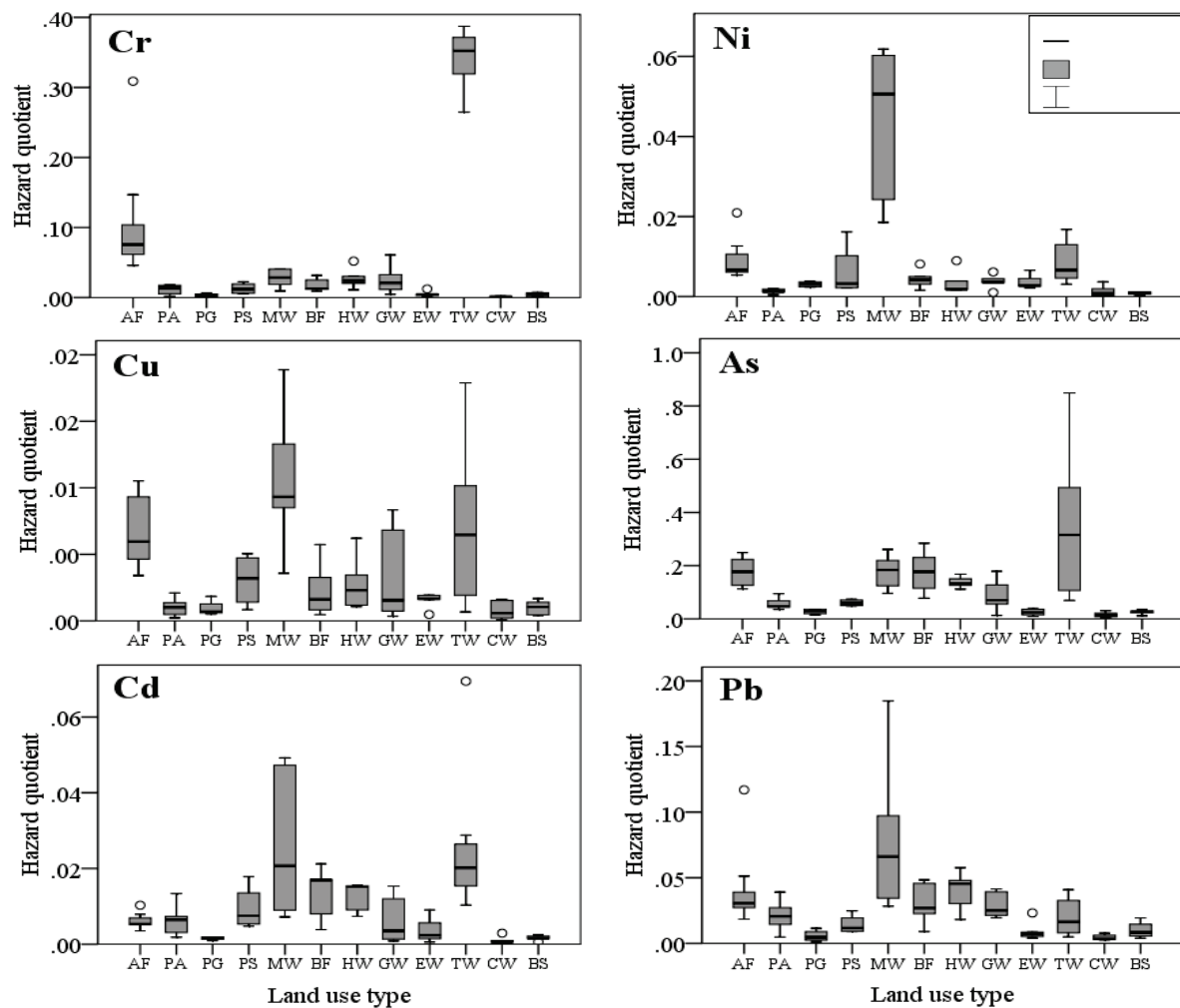
Figure 5-3. Hazard quotients (HQs) of trace metals in soils of different land uses in Dhaka City, Bangladesh through sum of ingestion, dermal contact and inhalation exposure pathways. Circle symbol represents outlier.

5.3.2.2 Carcinogenic risk of AS and Pb

The carcinogenic risk of As and Pb for adult inhabitants were estimated and presented in **Table 5-2**. Considering the exposure pathways, carcinogenic risk followed the descending

order of ingestion > dermal contact > inhalation. Site specific carcinogenic risk assessment showed higher risk of As for TW and Pb for MW site (**Table 5-2**). The range of carcinogenic risk for As was (3.0×10^{-6} to 6.6×10^{-5}), (2.8×10^{-9} to 6.2×10^{-8}) and (5.5×10^{-10} to 4.2×10^{-8}) and Pb (6.4×10^{-8} to 1.2×10^{-6}), (1.5×10^{-10} to 2.7×10^{-9}) and (4.3×10^{-12} to 3.6×10^{-10}) for ingestion, dermal contact and inhalation, respectively (**Table 5-2**). In general, the excess cancer risks lower than 10^{-6} are considered to be negligible, cancer risks above 10^{-4} are considered unacceptable (USEPA, 1989; Guney et al., 2010) and risks lying between 10^{-6} and 10^{-4} are generally considered an acceptable range (Fryer et al., 2006; Hu et al., 2012). The sum of Pb risks from the three exposure pathways for all the sites were less than 10^{-6} and regarded as negligible. While, the sum of risks for As were within the acceptable range of 10^{-6} to 10^{-4} for all the site, those for some sites such as TW were relatively close to the unacceptable level of 10^{-4}. Therefore, based on the results of the present study, the potential health risk for target population due to metal exposure through soil should not be overlooked considering the fact that dietary exposure is not taken into account in this study.

Table 5-2. Carcinogenic risk of arsenic and lead due to ingestion, dermal contact and inhalation of the adult inhabitants in Dhaka City, Bangladesh.

Land use type	Arsenic (As)				Lead (Pb)			
	Ingestion	Dermal	Inhalation	Sum of pathways	Ingestion	Dermal	Inhalation	Sum of pathways
AF	3.4E-05	3.2E-08	1.1E-08	3.4E-05	6.0E-07	1.4E-09	9.3E-11	6.0E-07
PA	1.1E-05	1.1E-08	5.9E-10	1.1E-05	3.1E-07	7.1E-10	8.0E-12	3.1E-07
PG	5.2E-06	5.0E-09	5.5E-10	5.3E-06	8.2E-08	1.9E-10	4.3E-12	8.2E-08
PS	1.2E-05	1.1E-08	7.3E-09	1.2E-05	2.1E-07	4.8E-10	6.5E-11	2.1E-07
MW	3.4E-05	3.2E-08	2.2E-08	3.4E-05	1.2E-06	2.7E-09	3.6E-10	1.2E-06
BF	3.4E-05	3.2E-08	2.1E-08	3.4E-05	4.3E-07	1.0E-09	1.4E-10	4.4E-07
HW	2.6E-05	2.5E-08	8.3E-09	2.6E-05	5.8E-07	1.3E-09	9.0E-11	5.8E-07
GW	1.7E-05	1.6E-08	5.2E-09	1.7E-05	4.2E-07	9.6E-10	6.5E-11	4.2E-07
EW	4.7E-06	4.5E-09	1.5E-09	4.7E-06	1.4E-07	3.2E-10	2.2E-11	1.4E-07
TW	6.6E-05	6.2E-08	4.2E-08	6.6E-05	2.9E-07	6.7E-10	9.0E-11	2.9E-07
CW	3.0E-06	2.8E-09	9.4E-10	3.0E-06	6.4E-08	1.5E-10	1.0E-11	6.5E-08
BS	4.8E-06	4.5E-09	1.5E-09	4.8E-06	1.5E-07	3.4E-10	2.3E-11	1.5E-07

5.4 Conclusions

This study showed that the soils from some land-uses in Dhaka City were heavily contaminated with toxic trace metals when they were compared with soil quality standards

such as Dutch soil quality standard. This study also indicated that both non-cancer and cancer risk for local residents and workers from ingestion, dermal contact inhalation exposures to contaminated soils were still within the acceptable range. However, when we consider the dietary exposure of metals, the public health risk will be more severe. Finally, this study recommends further research on different exposure media and epidemiologic investigations with a large number of participants in order to evaluate the actual health effects by toxic metals.

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Chapter 6

TRACE METALS IN SOIL AND VEGETABLES AND ASSOCIATED HEALTH RISK ASSESSMENT

Trace metals in soil and vegetables and associated health risk assessment

Abstract

The objective of this study was to assess the contamination level of trace metals in soil and vegetables, metal translocation and potential health risk to the urban population in Bangladesh. Soil in the agricultural fields were found to be notably contaminated with trace metals as the mean concentrations of Cr, Ni, Cu, As, Cd, and Pb were 384, 192, 311, 64, 7.12, and 199 mg/kg, respectively. Sequential extraction tests revealed that the studied metals were predominantly associated with the residual fraction, followed by the organically bound phases. Concentrations of Cd and Pb in edible parts of most vegetables were higher than the maximum permissible levels. The findings of this study suggested that the agricultural fields around the industrial area in Bangladesh are contaminated with trace metals and attention should be given on the potential health risk to local residents through consumption of vegetables grown in these areas.

6.1 Introduction

Soil pollution is any undesirable change in the physical, chemical and/or biological characteristics of soil, which reduces the amount of cultivable land and habitation. Soil acts as a sink and also as a source of pollution with the capacity to transfer pollutants to the ground water and food chain, and then to the human and/or animals (Khan et al., 2010). Human health is intimately related to the quality of soil and especially to its degree of contamination (Romic and Romic, 2003; Velea et al., 2009). Contamination of agricultural soil by various metals or metalloids is a matter of increasing concern on a global scale. Soil is contaminated by the trace metals from the bedrock itself or anthropogenic sources like solid or liquid waste deposits, agricultural inputs and untreated or poorly treated fallout of industrial and urban emissions (Singh et al., 2005; Wilson and Pyatt, 2007; Khan et al., 2008; Tiwari et al., 2011; Rahman et al., 2012). Once trace metals are accumulated in soil or sediment, they pose potential risks to the ecosystem and also to human health through food chain (Muchuweti et

al., 2006) due to their non-biodegradable and persistent nature (Duruibe et al., 2007). Although metals like cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), selenium (Se) and zinc (Zn) are essential in human metabolism (Lokeshappa et al., 2012), excessive amount of metals beyond maximum permissible level causes number of cardiovascular, renal, neurological impairment as well as bone diseases and several other health disorders (WHO, 1998).

The consumption of metal contaminated vegetables is one of the most important pathways for trace metals to human (Sipter et al., 2008). This food chain translocation of trace metals is one of the consequences of metal contaminated soil (Khan et al., 2008; Nasreddine and Parent-Massin, 2002; Turkdogan et al., 2003). Vegetables grown on contaminated soil can take up heavy metals and accumulate them in their edible and non-edible parts at quantities high enough to cause clinical problems to both animals and human beings. Additionally, foliar uptake of atmospheric trace metals emissions has also been identified as an important pathway of trace metal contamination in vegetable crops (Salim et al., 1993). In many developing countries like Bangladesh, growing vegetables along the river banks passing through the urban area is a common practice. Such urban rivers have often been reported to be polluted by trace metals (Kashem and Shingh, 1999). Concentration of accumulated metals in different vegetables depend on soil composition, water, nutrient balance, as well as metal permissibility, selectivity and absorption ability of the species (Ahmad and Goni, 2010). Investigations on the accumulation of trace metals from vegetables grown around the industrial sites have revealed high levels of Ni, Pb and Cd (Ahmad and Goni, 2010). While a significant number of studies have focused on As in Bangladeshi vegetables (Alam et al., 2003; Das et al., 2004; Karim et al., 2008; Rahman and Hasegawa, 2011), studies on other metals in vegetables are limited (Alam et al., 2003; Rahman et al., 2013). A recent study by Rahman et al. (2013) demonstrated that home grown Bangladeshi vegetables from As-contaminated area are likely to be important sources of As and heavy metals to humans. In this context, risks associated with the consumption of contaminated food grown near the industrial area are a potential health concern. The exchangeable fraction of metals is considered to be readily mobile and bioavailable, while metals incorporated into the crystal lattice of clays appear to be relatively inactive (Kashem et al., 2007). Other forms of trace metals in soils precipitated as carbonate, occluded in Fe–Mn and Al oxides or complexed with organic matter are considered to be relatively active fractions, depending upon the specific combination of physical and chemical properties of soil (Kashem et al., 2007). However, no detailed study on geochemical fractionation of agricultural soils concerning trace metals in

soils and vegetables in the urban areas have been conducted yet. So, it is a nerve-racking issue to find out the present status of toxic metals in the surface soil, redress the affected subsequent environmental problems and adopt a future mitigation strategy. Therefore, the present study aims to investigate the contamination levels of six global warning trace metals (Cr, Ni, Cu, As, Cd and Pb) in soil and vegetables; to evaluate the translocation behavior of trace metals in vegetable species; and to assess the health risks to the local residents via the consumption of selected vegetables in the urban areas in Bangladesh.

6.2 Materials and methods

6.2.1 Study area

The Dhaka City, located at the centre of Bangladesh is one of the most densely populated cities in the world, home to approximately twelve million people (Ahmad et al., 2010; Mohiuddin et al., 2011). The metropolitan area of Dhaka is about 815.8 km^2. Agriculture fields from nine sites were selected around the industrial areas of Dhaka City, located besides three rivers, i.e., Turag, Buriganga and Shitalakha (**Figure 6-1**). Areas were selected based on farmer's interview where irrigation with contaminated river water has been a common practice for many years. Numerous industries (leathers, textiles, metals processing, paper mills, electronic goods, power plant, fertilizers, pharmaceuticals, dyeing, battery manufacturing, ink manufacturing, Pb-Zn melting, brick fields, etc.) are situated near the selected fields (Rahman et al., 2012). Most of the treated and untreated industrial effluents are discharged to these rivers. During dry season, the local farmers incorporate polluted sediment to the agricultural fields as organic matter supply. Moreover, several acres of agricultural land are irrigated with contaminated river. Farmers cultivate different types of vegetable crops in these lands. As per the information given by the local farmers we have identified the above area where, the basic information's of the study areas are presented in **Table 3-1**.
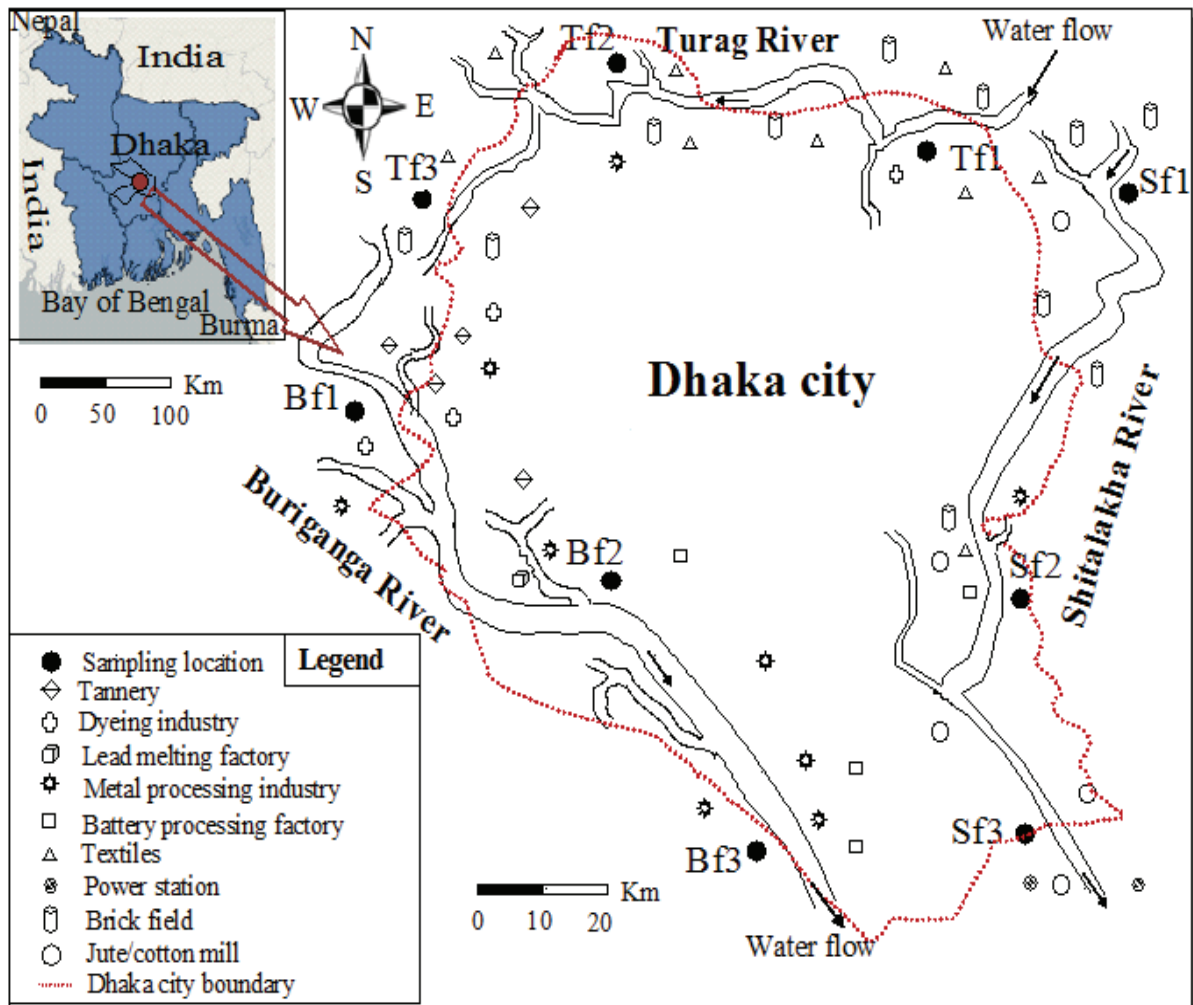
Figure 6-1. Map of the sampling location of agricultural fields around Dhaka city, Bangladesh.

6.2.2 Soil and vegetable sampling

Soil and vegetable samples were collected from nine sampling stations around the urbanized industrial area during February and March, 2012. At each sampling station, soil samples from the top 20 cm were collected in sub-samples maintaining a distance of about 20 m (Xu et al., 2013) from one sub-sampling point to another. Sub-samples from five points were thoroughly mixed to form a composite sample and four composite samples were obtained from each sampling station. A total of 36 samples of four different vegetable species i.e. Brinjal (*Solanum melongena*), Bottle gourd (*Lagenaria siceraria*), Pumpkin (*Cucurbita maxima*) and Tomato (*Solanum lycopersicum*) were collected from the same sites. Soil samples were air-dried at room temperature, then grounded and homogenized. Each vegetable sample was carefully washed with distilled water and the edible parts were cut into small pieces and then

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oven dried at 70–80 °C to attain constant weight (Tiwari et al., 2011). The moisture contents were calculated from the fresh and dry weights. The dried soil and vegetable samples were crumbled and pulverized with a porcelain mortar and pestle and sieved through 2 mm nylon sieve. The processed samples were brought to Yokohama National University, Japan, for chemical analysis.

6.2.3 Sample analysis

For total metal analysis, 0.2 g of the soil and 0.3 g vegetables samples were treated with 1.5 ml 69% HNO_3 (Kanto Chemical Co, Japan) and 4.5 mL 35% HCl (Kanto Chemical Co, Japan) in a closed Teflon vessel and was digested in a Microwave Digestion System (Berghof Speed wave[®], Germany). Detailed analysis procedures are presented in **chapter 5**. For chemical partitioning of metals, soil samples were analyzed using Tessier sequential chemical extraction procedure which helps to evaluate the mobility of metals (Tessier et al., 1979). The detailed geochemical fractionation procedure of soil is presented in **Table 2-1**.

6.2.4 Instrumental analysis and quality control

For trace metals, samples were analyzed using inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700 series). Multi-element Standard XSTC-13 (Spex CertiPrep[®] USA) solutions was used to prepare calibration curve. The calibration curves with $R^2 > 0.999$ were accepted for concentration calculation. Detailed procedure of quality controlled was explained in the previous research by Islam et al. (2014).

6.2.5 Statistical analysis

The data were statistically analyzed using the statistical package, SPSS 16.0 (SPSS, USA). The means and standard deviations of the metal concentrations in soil and vegetables were calculated. A Pearson bivariate correlation was used to evaluate the inter-element relationship in soil. Multivariate Post Hoc Tukey tests were employed to examine the statistical significance of the differences among mean concentrations of trace metals among vegetables and sites.

6.3   Results and discussion

6.3.1 Chemical properties and metal concentrations in soil

The concentration of total trace metals (Cr, Ni, Cu, As, Cd and Pb) in different soil samples are presented in **Figure 6-2** and **Table D.1**. The order of average concentrations of trace

metals in surface soils were found as Cr > Cu > Pb > Ni > As > Cd. The highest mean concentration of Cr (1120 mg/kg) was found at Bf1 site, Ni (442 mg/kg) and Cd (12.3 mg/kg) at Bf3 site, Cu (510 mg/kg), As (90.4 mg/kg) and Pb (567 mg/kg) at Bf2 site, respectively (**Figure 6-2**). High levels of these metals were observed at Bf1, Bf2 and Bf3 sites, due to the effects of various industries. The notable industrial activities observed at these sites were tanneries, lead smelting, battery manufacturing, metal processing etc. Solid and liquid wastes emanating from the tanning industries contain various toxic trace metals (McMartin et al., 1999). About 270 tanneries have been operating their activities covering an area of 4 km^2, producing approximately 15000 m^3 of untreated chemical wastes and discharged to the low-lying areas, natural canals and other water bodies such as the Buriganga and Turag rivers. These are major sources of water supply for agricultural activities (Arias-Barreiro et al., 2010; UNIDO, 2000). Severe metal pollution from metal processing, battery manufacturing and smelting industries- has been reported in many countries (Martley et al., 2004; Rawlins et al., 2006). The highest concentration of Cd (12.3 mg/kg) was found at Bf3 sites, which are mostly used for industries like galvanization and alloy, paints, batteries and catalyst. Used metal fittings, rubber, plastics, tires, paints, etc. are materials which are responsible for emitting Cd to the environment. During sampling, leachates were observed from defused Ni-Cd batteries, Cd plated items, casting lead and lead products manufacturing at these sites. A high level of Pb (268 mg/kg) was found near battery manufacturing facilities, which were suspected to pollute the soil in the industrial area of Baoji city, China (Li and Huang, 2007).

Table 6-1. Chemical properties in soil at different sites of the study area, Bangladesh.

Sites	pH	Ec (mS/m)	% C	% N
Tf1	5.1	42	3.6	0.22
Tf2	6.6	19	1.3	0.15
Tf3	6.4	12	0.55	0.067
Bf1	5.7	7.3	0.53	0.069
Bf2	5.2	20	0.77	0.10
Bf3	5.8	121	4.3	0.39
Sf1	6.0	9.6	0.67	0.081
Sf2	6.4	12	0.62	0.084
Sf3	6.0	15	0.96	0.14

It was noted that Ni, Cd and Pb are the main primary raw materials used for battery production (Li and Huang, 2007). Earlier studies reported that huge amount of Cu is released from steel manufacturing industry (Srinivasa et al., 2010), Cr from tannery industry (Nath et

al., 2009), Pb from smelting, motor-vehicle exhaust fumes and from corrosion of lead pipe work. Textile industries can also act as one of the major sources of metal pollution in the environment (Kashem and Singh, 1999). In the present study, different industrial activities were the dominant source of metal pollution. High levels of trace metals in the affected soils were consistent with the patterns observed at the industrial area of Dhaka Export Processing Zones (Rahman et al., 2012).

The mean concentrations of metals in the present study were above the Dutch soil quality standard (VROM, 2000), Canadian Environmental Quality Guidelines (CCME, 2003) and Australian Guideline on the investigation levels for soil (DEP, 2003). The mean concentration of Cr, Ni, Cu, As, Cd and Pb in soils (384, 192, 311, 64, 7.12 and 199 mg/kg, respectively) also exceeded the Dutch Target Value (**Table D.2**). These types of land use soil samples were considered as moderately contaminated. The Cd pollution was the most serious among the studied metals as the mean concentration of Cd was more than 8 times higher than Dutch Target Value (**Table D.2**).
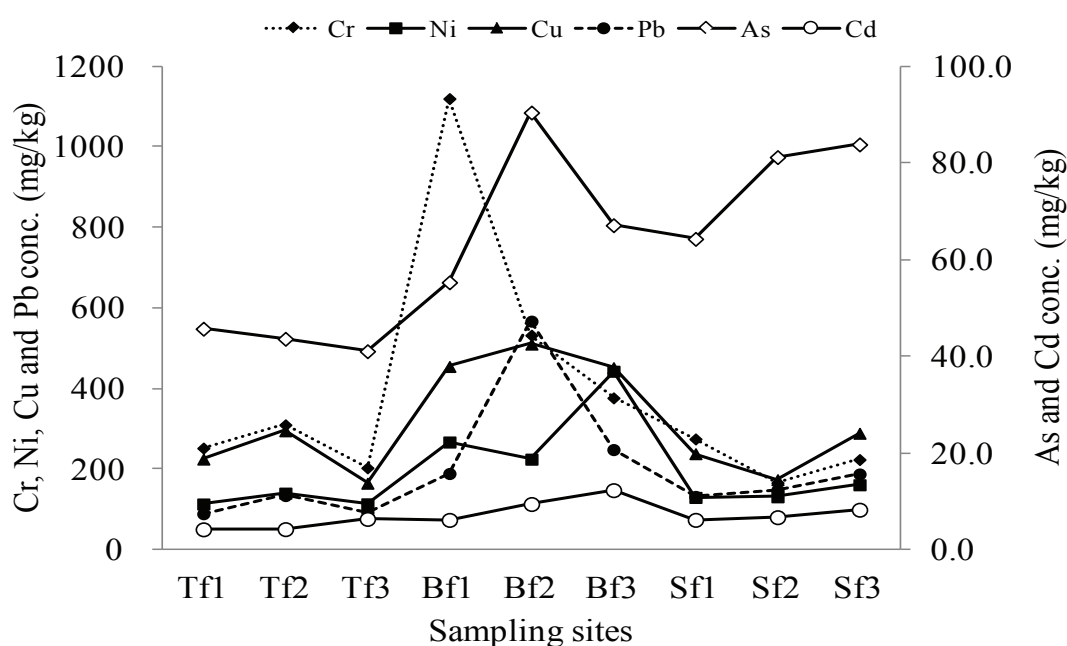
Figure 6-2. Total metal concentration (mg/kg) in soil at different sampling sites.

In Bangladesh, the agricultural soil is contaminated with trace metals through the repeated use of wastewater from industries and other sources in irrigation as well as application of chemical fertilizers and pesticides. Cadmium, for example, is found in wastewater and also in phosphatic fertilizers due to the presence of Cd as an impurity in all

phosphate rocks (Ahmad and Goni, 2010). Cadmium concentration in the present study was lower than the study conducted around the Dhaka Export Processing Zone (DEPZ), by Ahmad and Goni (2010).

The DEPZ is a large industrial area comprised of a large number of local and foreign industries like fabric printing and dyeing, food processing, textiles, electric cables, pharmaceutical, chemical, etc. that contribute to the discharge of Cd in soil. The metal concentrations in the present study were about 10 times higher than the findings of Rahman et al. (2013) who reported severe As contamination in rural area (**Table D.2**). However, these soils might pose serious contamination due to the use of untreated industrial waste for crop production. With regard to agricultural soil, the major input of trace metals are the application of agrochemicals and other soil amendments (Wong et al., 2002). Pearson's correlation coefficients for the investigated metals are depicted in **Table 6-2**. Inter metal interactions may illustrate the sources and pathways of the metals present in soil. A clear pattern of strong association was found among the metal pairs in the soil samples: Cr-Cu, Ni-Cu, Ni-Cd, Cu-Pb and As-Pb. These strong correlations among metal-metal pair may be an indication of common sources of these metals as well as similar geochemical characteristics. The correlations of some of the metal pairs were similar in soil and sediment samples indicating is correlation between agriculture contamination and nearby rivers.

Table 6-2. Correlation coefficients among trace metals and chemical properties in soil (n=36).

Metals	Cr	Ni	Cu	As	Cd	Pb	pH	Ec	%C	%N
Cr	1									
Ni	0.436	1								
Cu	0.699*	0.763*	1							
As	-0.031	0.225	0.359	1						
Cd	0.056	0.806**	0.587	0.605	1					
Pb	0.303	0.406	0.769*	0.671*	0.588	1				
pH	-0.341	-0.255	-0.509	-0.226	-0.204	-0.495	1			
Ec	-0.091	0.791*	0.364	0.003	0.66	0.113	-0.24	1		
%C	-0.166	0.523	0.178	-0.192	0.321	-0.078	-0.408	0.892**	1	
%N	-0.159	0.688*	0.301	-0.04	0.533	0.028	-0.253	0.967**	0.946**	1

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

6.3.2 *Geochemical fractionations of metals in soil*

The mobility and toxicity of metals are mainly dependent on metal speciation in the environmental media. The relative distribution of trace metals in different fractions are shown in (**Figure 6-3** and **Table D.1**). In general, the results indicated that Cr, Ni, Cu, As, Cd and Pb were predominantly associated with the residual fraction followed by the organically bound phases. These two fractions accounted for more than 71%, 73%, 66%, 58%, 70% and 68% of the total concentrations in soil. In this study, the residual phase is believed to consist mainly of primary and secondary minerals, which hold metals within their crystalline structure (Murray et al., 1999; Szolnoki and Farsang, 2013). As shown in the **Table D.1**, the level of Cu (165 to 510 mg/kg) at the study fields was extremely high. Considering the average percentage of exchangeable and carbonate bound fraction, Cu was significantly ($P > 0.05$) higher than the other metals, implying that Cu is more mobile and phytoavailable. In the case of Cu, the organic bound fraction (coinciding with organic matter and sulphides) was also noticeable (34 % of the total content). These findings are in agreement with the results obtained by several authors (Morillo et al., 2004; Wang et al., 1998) who found high proportions of Cu in the organic bound fraction due to the high stability of the organic Cu complexes. Metals present in the exchangeable, carbonates and Fe-Mn oxides bound fractions may become available to plants upon solubilization. The relative proportion of mobile Cd (exchangeable + carbonates + Fe-Mn oxides fraction) in the soil was 36%, indicating surface soil contamination with Cd originating from anthropogenic activities. These observations are in agreement with the result of Chlopecka et al. (1996) who reported that metals from anthropogenic sources are more mobile than those derived from parent materials. In comparison with other metals, Cd displayed a distinct character in the soil, where associated with the residual fraction, which reached 19% at Bf2 site to 67% at Tf1 site of total Cd content, followed by the organically bound phase with 17% at Tf1 site to 55% at Bf2 site of total in soil (**Figure 6-3**). From these contaminated rivers, water was used as irrigation to produce vegetables. In this way, some readily soluble elements at some sites would enter the soil with the irrigation water. As for Cr, Ni and Pb, in the soil of the selected fields, they were mainly bound to the residual fraction, followed by the Fe-Mn oxides or organically bound phases (**Figure 6-3**).
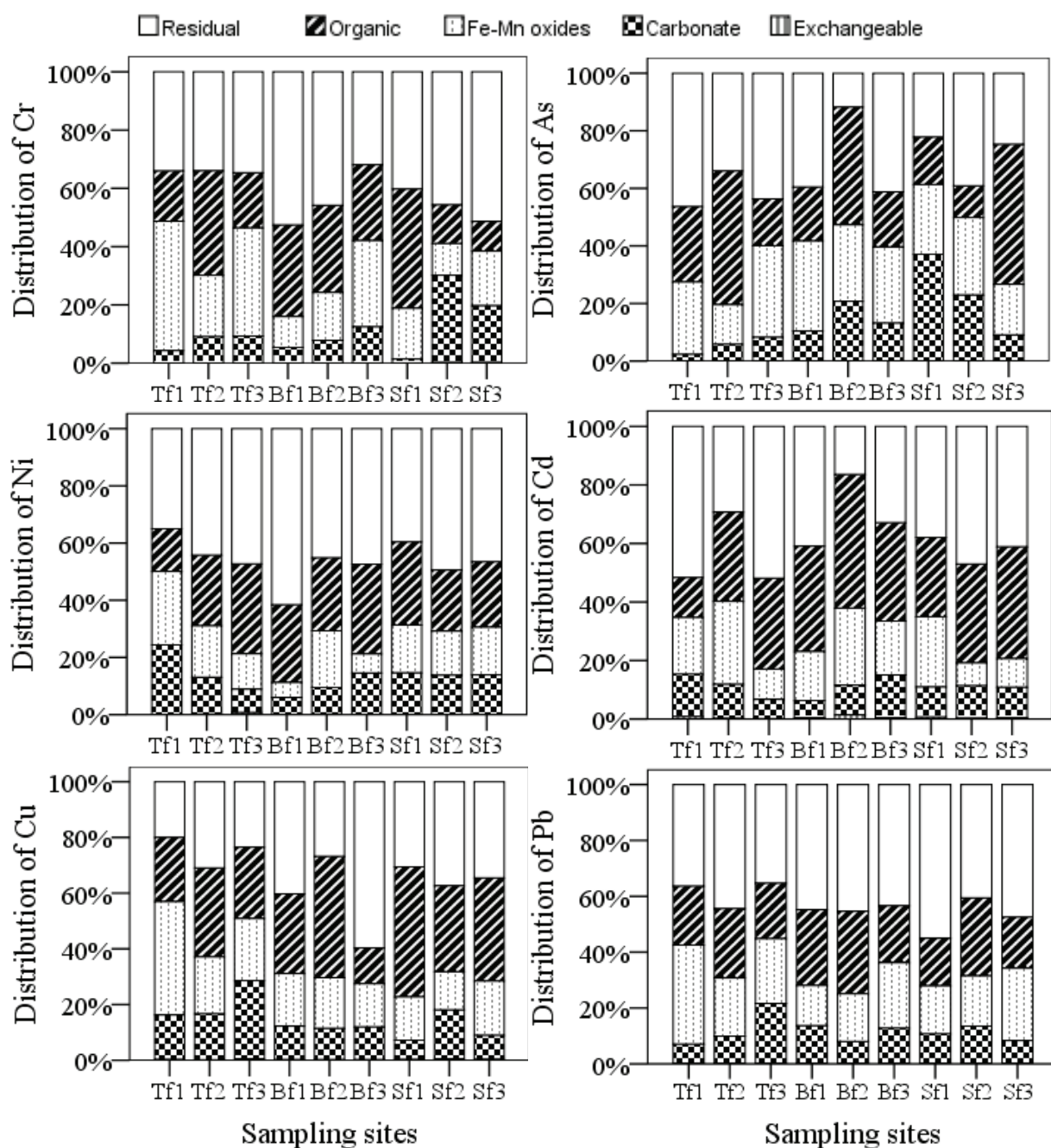
Figure 6-3. Chemical speciation of trace metals in soil of different sampling sites of agricultural fields.

6.3.3 Trace metal concentrations in vegetables

The concentrations of trace metals (mg/kg fw) in the edible parts of vegetables found in the present study are listed in **Table D.3**. The concentrations of metals varied greatly among plant species and sample locations. The average concentration of trace metals in all vegetable samples were in the following order: Cu > Ni > Pb > Cr > Cd > As. Chromium concentrations

in the edible parts of some vegetables were higher than the FAO & WHO permissible limits. Ni for all sites and Cu for some sites exceeded the Chinese food safety standards value, where as it was lower than the permissible levels in food as per FAO & WHO guidelines. The concentration of Pb in vegetables for all sites exceeded the food safety standards in China and the permissible levels in food as per FAO & WHO guidelines (**Table D.3**). Among the studied vegetables, brinjal (*S. melongina*) accumulated much higher amounts of trace metals (0.84, 3.1, 16, 0.14, 0.42 and 0.75 mg/kg fw for Cr, Ni, Cu, As, Cd and Pb, respectively) than the other vegetables (**Figure 6-4**). Cadmium concentration in *S. melongina* (0.42 mg/kg fw) was significantly ($p > 0.05$) higher than other three vegetables (0.06, 0.02 and 0.11 mg/kg fw for *L. siceraria*, *C. maxima* and *S. lycopersicum*, respectively). There were significant ($p > 0.05$) difference between the agricultural fields of Turag and Buriganga as well as Buriganga and Shitalakha for Cr, Cu and Pb concentration in vegetables (**Table D.3**). This implied that vegetables cultivated in the fields besides the Buriganga River were more contaminated by trace metals and the studied vegetables were severely polluted than the vegetables from the other two riverside fields. Among the vegetables, the highest mean concentration of Pb was found in *L. siceraria* (2.2 mg/kg fw) collected from sites of Buriganga River. The higher concentration of Pb in this species could probably due to the lead melting activity beside the Buriganga River. When melting and other industrial activities started, heavy smoke containing various kinds of trace metals, metalloids and organic pollutants would have been discharged into the air and the vegetables growing on these sites could well have been the first recipients of these substances (Bi et al., 2009; Luo et al., 2011). A major pathway for Pb may enter the above-ground tissues of plants is through foliar deposition (Xu et al., 2013). Our observations revealed pronounced Pb concentration in the four studied vegetable species at Bf1, Bf2 and Bf3 sites. Burning of industrial waste, coal in the brick fields and power station were observed at these sites, which might result to the deposition of particulate matter (PM) on vegetables. Thus, the vegetables were exposed to fine particles of Pb from $PbSO_4$, PbO and $PbCO_3$. Uzu et al. (2011) showed that PM deposited on plant leaves and penetrate inside the plant tissues.
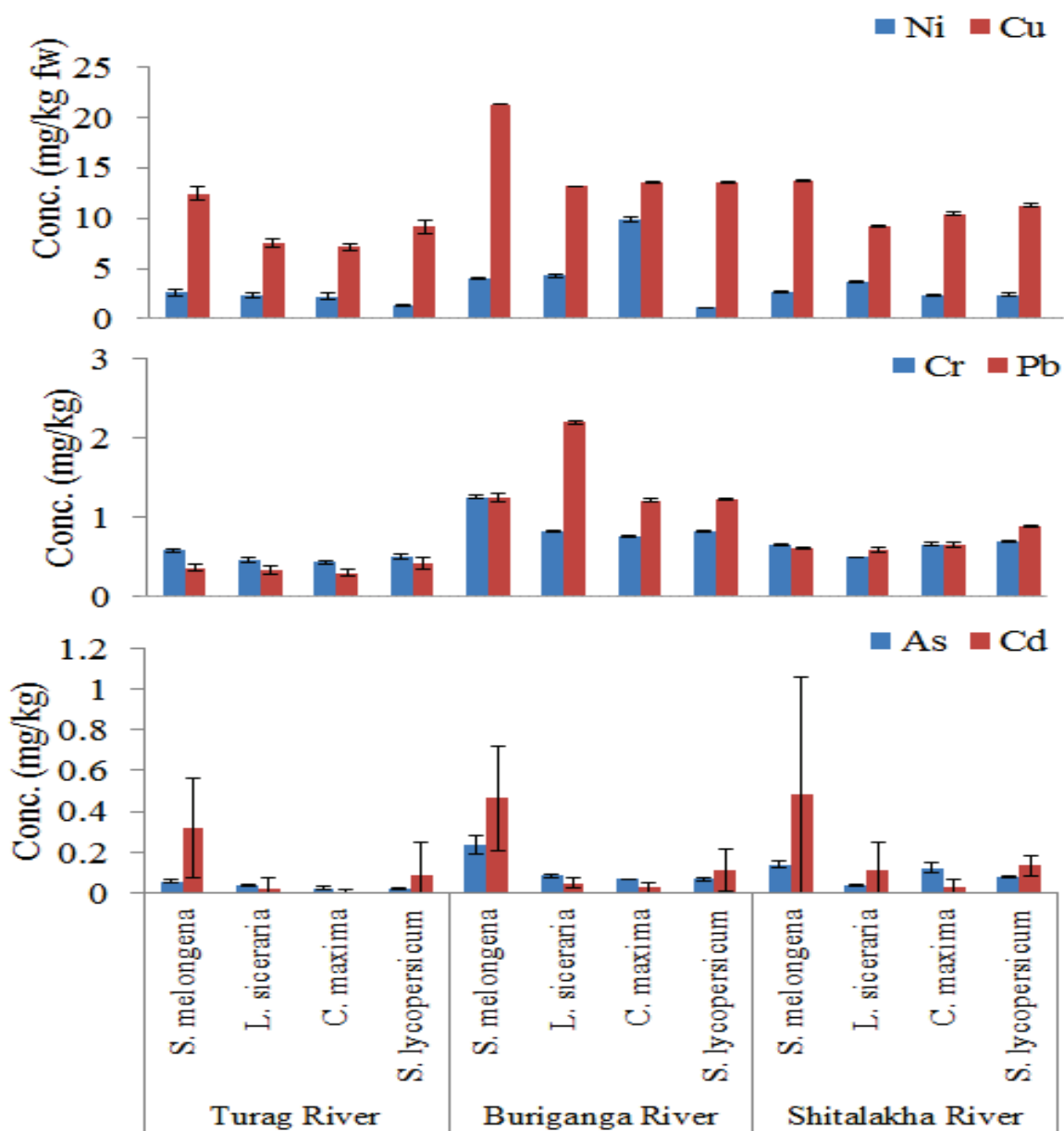
Figure 6-4. Metal concentration (mg/kg fw) in vegetables at three riverside agricultural fields around the industrial area in Dhaka City, Bangladesh. Error bar represent ±SD.

Correlation analysis of metal concentrations between vegetables species and soil indicated the significant relationship between bottle gourd-soil, pumpkin-soil and tomato-soil for Cr, Ni and Pb. Meanwhile, no relationship was observed between brinjal and soil for the studied metals (**Table 6-3**).

Table 6-3. Correlation of metals between soil (total metal) and vegetable samples.

Metal	Soil-brinjal	Soil-bottle gourd	Soil-pumpkin	Soil-tomato
Cr	0.538	0.714*	0.474	0.418
Ni	0.422	0.359	0.790*	-0.353
Cu	0.55	0.665	0.654	0.366
As	0.109	0.569	0.382	0.459
Cd	0.31	0.356	0.545	-0.03
Pb	0.433	0.954**	0.938**	0.865**

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

6.3.4 Transfer of metals from soil to vegetables

The transfer factor (TF) was calculated for each vegetable at each site separately. Transfer factor can be used to evaluate the capability of plants to transfer metals from soil to edible tissues and is one of the key components controlling human exposure to metals through the food chain. Transfer factor (TF) was calculated as follows:

$$TF = \frac{C_{plant}}{C_{soil}} \qquad (1)$$

Where, C_{plant} and C_{soil} represent the total trace metal concentration in the edible parts of vegetables and total or fractionated metal concentration in soils on a dry weight basis, respectively (Khan et al., 2010; Li et al., 2012).

The accumulation of metals in the edible parts of vegetables could have a direct impact on the health through food chain. Metals with high TF are more easily transferred from soil to the edible parts of plants than the ones with low TF. As seen from **Table D.4** and **Figure 6-5**, large variations in TFs based on total soil metal concentration were observed among different vegetables and metals. The average TF of trace metals in all crops were in the following order: Cu > Cd > Ni > Pb > Cr > As. Among the six metals the highest mean TF (0.64) was for Cu ranging from 0.27 to 1.5. The TF for Cu was 10, 19 and 35 times higher than that of Pb, Cr and As. Generally, the TF of trace metal is controlled by the chemical speciation in soil, soil properties, such as pH and salinity, and crop genetic features (Peris et al., 2007; Li et al., 2012).

The transfer of metals from soil to vegetables is thought to decrease approximately in the order of the extraction sequence, from readily available to unavailable, because the

strength of extraction reagents used increases in this sequence (Tessier and Campbell, 1987). Hence, the exchangeable fraction may indicate the form of the metals that are most transferable from soil to vegetables. Transfer factors of the studied metals were found in the following order: exchangeable > carbonate > Fe-Mn oxides > organic > residual. In the exchangeable fraction, the mean TFs of Cr (30, 22, 23 and 25), Ni (16, 19, 23 and 10), Cu (30, 23, 23 and 25), As (29, 18, 27 and 18), Cd (16, 2.6, 0.63 and 4.1) and Pb (33, 41, 33 and 41) for *S. melongena*, *L. siceraria*, *C. maxima* and *S. lycopersicum*, respectively (**Table D.4**). The second step extracts metals bound to carbonate and specifically adsorbed phases, which can easily become mobile and available to plants. The remaining three fractions (Fe-Mn-oxides, organic/sulphide and residual) are generally strongly held within the soil constituents and have lower transferability (**Table D.5**). The present study showed that, weakly bound fractions (exchangeable and carbonate) were the best for Cu and Pb to estimate metal transfer in vegetables as its coefficient of variation was minimal among the TFs calculated using different extraction fraction, whereas any TFs did not perform well for the other metals (**Table D.4**). It is suggested that either fractionation is not a good indicator of bioavailability or air, not soil, may be a major pathway for the metal transfer to vegetables.
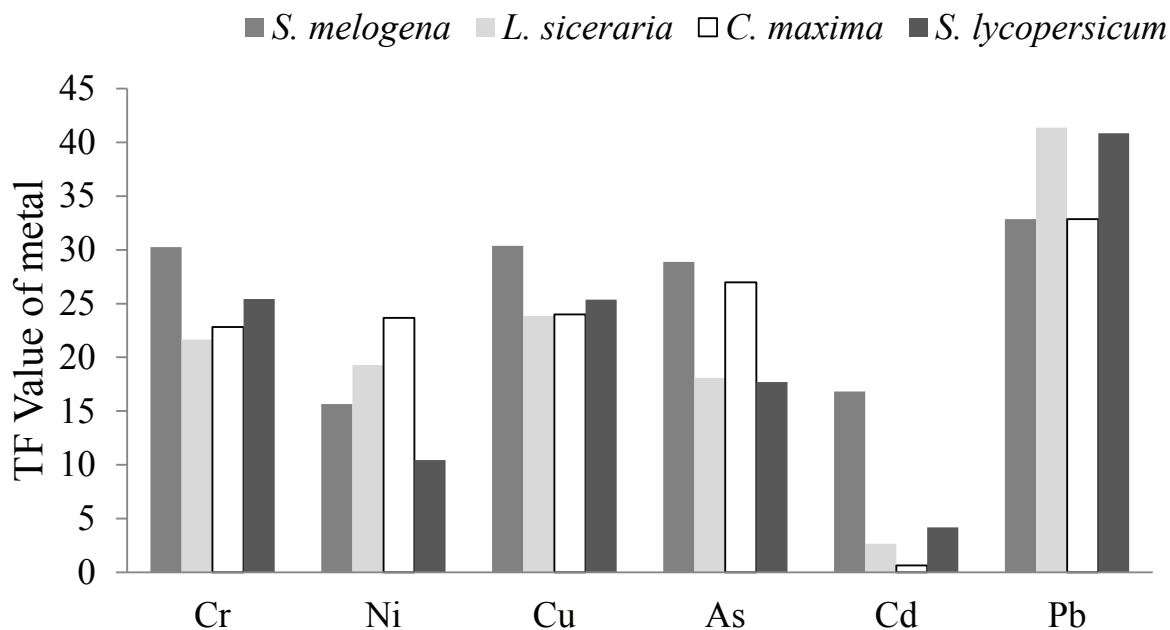
Figure 6-5. Transfer factor (TF) values of metals (exchangeable + carbonate fractions) from soil to vegetables.

6.4 Conclusions

This study showed that the intensive uncontrolled operation of various industries has resulted in the release of trace metals in the local environment, and caused elevated concentrations of trace metals in the surrounding soil. The concentrations of trace metals in soils from all sites exceeded the soil quality standards, indicating high risk to the surrounding ecosystems. Vegetables grown in the nearby sites were also contaminated by the relevant metals, especially Cu, Cd and Pb, which could be a potential health concern to the local residents. Considering the transfer of metals from soil to vegetables, Cu and Pb were indicated to have higher TF values (based on total soil concentration) than the other metals. Discharge of industrial waste to the nearby agricultural fields could be stopped and for the remediation of pollution in a sustainable and eco-specific way. Moreover, different remediation measures should be taken promptly to remove excising metal contamination. Further studies are needed in order to assess the metal concentrations in human beings (blood and urine) and animals and to identify sources of trace metals of the study area.

Acknowledgments

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Chapter 7

MONITORING OF TRACE METALS IN FOODSTUFFS GROWN AROUND THE INDUSTRIAL AREA OF DHAKA CITY, BANGLADESH AND HEALTH RISK ASSESSMENT

Monitoring of trace metals in foodstuffs grown around the industrial area of Dhaka City, Bangladesh and health risk assessment

Abstract

Dietary exposure to trace metals is a matter of concern for human health risk through the consumption of rice, vegetables and other major foodstuffs. In the present study, we investigated the levels of chromium (Cr), nickel (Ni), copper (Cu), arsenic (As), cadmium (Cd) and lead (Pb) in eight group of foods, namely, cereals, pulses, vegetables, fruits, fish, meat, egg and milk. The mean concentrations of Cr, Ni, Cu, As, Cd and Pb in the foodstuffs were 1.7, 1.8, 5.5, 0.20, 0.06 and 0.63 mg/kg fw, respectively. The daily intakes (EDIs) of Cr, Ni, As, Cd and Pb were higher than the maximum tolerable daily intake (MTDI), indicating the potential sources from dietary intake. From the human health point of view, this study showed that studied foods were not safe for the local inhabitants and potential risk cannot be neglected for regular or excessive consumers.

Keywords: Trace metals, food chain, dietary intake, health risk, Bangladesh.

7.1 Introduction

Metals and metalloids are ubiquitous in the environment originates from natural or anthropogenic intervention and their elevated concentrations in the environment through waste disposal, smelter stacks, atmospheric deposition, application of fertilizer, pesticide and sewage sludge in the arable land (Cui et al., 2005; Zheng et al., 2007). In addition to their essentiality for plant growth and/or human nutrition, some micronutrients (e.g. Cu, Cr and Ni) might be toxic at high concentrations (Mc Laughlin et al., 1999; Rahman et al., 2014). Other trace elements, such as As, Cd and Pb might also in advertently enter the food chain and pose risk to human and animals (Sankar et al., 2006; Sharma et al., 2007; Bundschuh et al., 2012; Ji et al., 2013; Rahman et al., 2014). Trace metals such as Cr, Ni, As, Cd and Pb have been considered as the most toxic elements in the environment by the US Environment Protection Agency (USEPA) (Cameron, 1992; Lei et al., 2010). Therefore, the risks associated with metal contamination in foodstuffs are of great concern.

Although the relative contribution of trace metals has not yet been clearly established, the dietary intake is considered as the vital exposure pathway (Kachenko and Singh, 2006; Sharma et al., 2007). **Figure 7-1** shows those possible food chain pathways through which Bangladeshi population are generally being exposed to metal toxicity. Human, one of the topmost consumer of the ecosystem, uptake various metals from contaminated rice, vegetables, fish, milk and meat hence 'soil–plant–human' and/or 'plant–animal–human' could be the potential food chain pathways of metal accumulation in human. In this study we tried to trace food chain pathways of natural ecosystem through which metals may enter into human body so that we can assess the potentiality of these pathways in exposing human to trace metals.

Rice is the major staple food in many countries, particularly in Asian countries like Bangladesh, India, Thailand, China and Vietnam where soil and ground water pollution with high level of As and trace metals have been reported (Roychowdhury et al., 2003; Duxbury et al., 2003; Meharg and Rahman, 2003; Das et al., 2004; Rahman et al., 2013). Increased levels of trace metals in agricultural soils and its uptake in rice, vegetables and other food crops has become a real health issue in this region (Meharg and Rahman, 2003; Williams et al., 2006). While, a significant number of studies have been focused on As in Bangladeshi rice and vegetables (Alam et al., 2003; Das et al., 2004; Karim et al., 2008; Rahman and Hasegawa, 2011), studies on other trace metals in other daily consumable foods are scarce (Alam et al., 2003; Rahman et al., 2013). Therefore, this study aimed to evaluate the levels of trace metals in foodstuffs that are consumed by Bangladeshi population, and to assess health risk associated with dietary intake of metals.
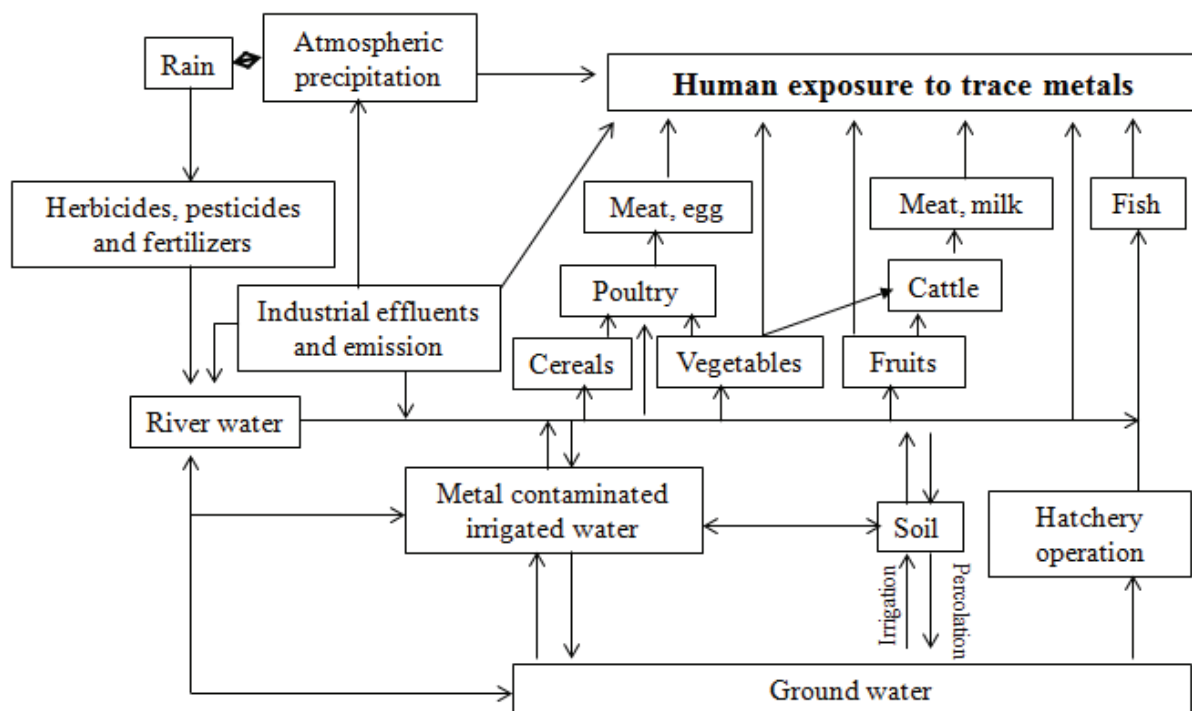
Figure 7-1. Possible food chain pathways through which humans may be exposed to trace metals (modified after Rahman et al., 2008).

7.2 Materials and methods

7.2.1 Study area and sample

The most consumable foods for Bangladeshi people i.e. cereals, pulses, vegetables, fruits, fish, meat, egg and milk were collected during February-March, 2012 and August-September, 2013. About 173 food samples were collected from nine riverine ecosystems around Dhaka City urban area, Bangladesh (**Figure 7-2**). A composite sample for each food item was prepared and homogenized in a food processor and 50 g test portions were stored at -20 $^{\circ}$C in the laboratory of the Institute of Nutrition and food Science (INFS), University of Dhaka, Bangladesh. The processed samples were brought to Yokohama National University, Japan for chemical analysis.
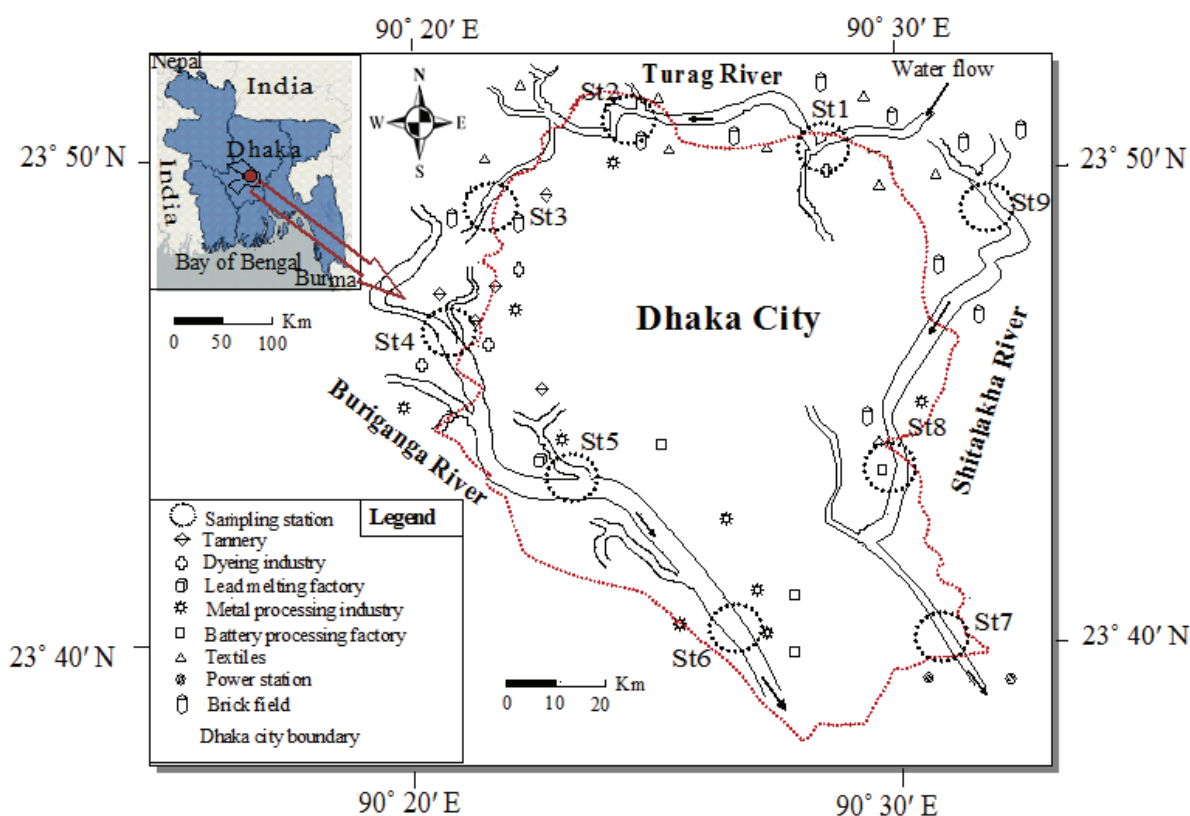
Figure 7-2. Map of the sampling sites of three riverside urban ecosystems around Dhaka City, Bangladesh.

7.2.2 Sample analysis

Detailed analysis procedures have been stated in **chapter 6.**

7.2.3 Instrumental analysis and quality control

Detailed procedure of quality controlled was explained in the previous research by Islam et al. (2014) and **chapter 4**.

7.2.4 Data calculation

7.2.4.1 Estimated daily intake of metals

The estimated daily intake (EDI) of trace metals through foodstuffs depend on metal concentrations (on fresh weight basis), daily vegetable consumption, as well as body weight, which was calculated with the following formula:

$$EDI = \frac{\sum FIR_i \times C_i}{BW} \qquad (1)$$

Where, *FIR* is the daily food consumption rate (on fresh weight basis) for adult residents is presented in **Table 7-2** [(questionnaire survey of this study and Report of the household income and expenditure survey 2010 (HIES, 2011)], in this study, we conducted 270 food consumption questionnaire surveys from 15 February to 15 March, 2012, i is food category, C is the metal concentrations (mg/kg fw) in foods and BW is the bodyweight of an adult resident was set to 60 kg in the present study (FAO, 2006).

7.2.4.2 Health risk assessment

In this study, the non-carcinogenic health risks associated with the consumption of foodstuffs by the local inhabitants were assessed based on the hazard quotients (*HQs*). This method of estimating risk using *HQ* was provided in the USEPA Region III risk-based concentration table (USEPA, 2000), and is based on the following equation:

$$HQ = \frac{EDI}{RfD} \times 10^{-3} \qquad (2)$$

Where *EDI* is the estimated daily intake of metal (mg/day) and *RfD* is the oral reference dose (mg/kg/day). The oral reference doses were based on 0.003, 0.02, 0.04, 0.0003, 0.001 and 0.004 mg/kg/day for Cr, Ni, Cu, As, Cd and Pb, respectively (JECFA, 1993). If the *HQ* is equal to or higher than 1, there is a potential health risk, and related interventions and protective measurements should be taken.

The target carcinogenic risks (TR) derived from the intake of As and Pb was calculated using the equation provided in USEPA Region III Risk-Based Concentration Table (USEPA, 2006):

$$TR = \frac{EFr \times ED \times EDI \times CSFo}{AT} \qquad (3)$$

Where, *EFr* is the exposure frequency (350 days/year), *ED* is the exposure duration (30 years) (USEPA, 2006) and *AT* is the averaging time for carcinogens (365 days/year × 70 years). *CSFo* is the oral carcinogenic slope factor from the Integrated Risk Information System (USEPA, 2010) database were 1.5 and 8.5×10^{-3} (mg/kg/day)$^{-1}$ for As and Pb.

7.2.4.3 Statistical analysis

The data were statistically analyzed using the statistical package, SPSS 16.0 (SPSS, USA). The means and standard deviations of the metal concentrations in foodstuffs were calculated. Multivariate Post Hoc Tukey tests were employed to examine the statistical significance of the differences among mean concentrations of trace metals among foodstuffs.

7.3   Results and discussion

7.3.1 Metal concentrations in foodstuffs

The concentrations of Cr, Ni, Cu, Zn, As, Cd and Pb (mg/kg fw) were determined in the most commonly consumed foods in Bangladesh (cereals, pulses, vegetables, fruits, fish, meat, egg and milk) and presented in **Figure 7-3** and **Table E.1**. Average concentration of trace metals showed the descending order of vegetables > fish > fruits > pulses > cereals > egg > meat > milk. For all types of foods, relatively large variations in metal concentrations were observed, even within the same kind of food. The observed variation in metal concentrations in foodstuffs could be due to variation in absorption and accumulation capabilities (Pandey and Pandey, 2009), growth period and stages of food crops (Saha and Zaman, 2013) and climatic differences of the study areas (Santos et al., 2004).
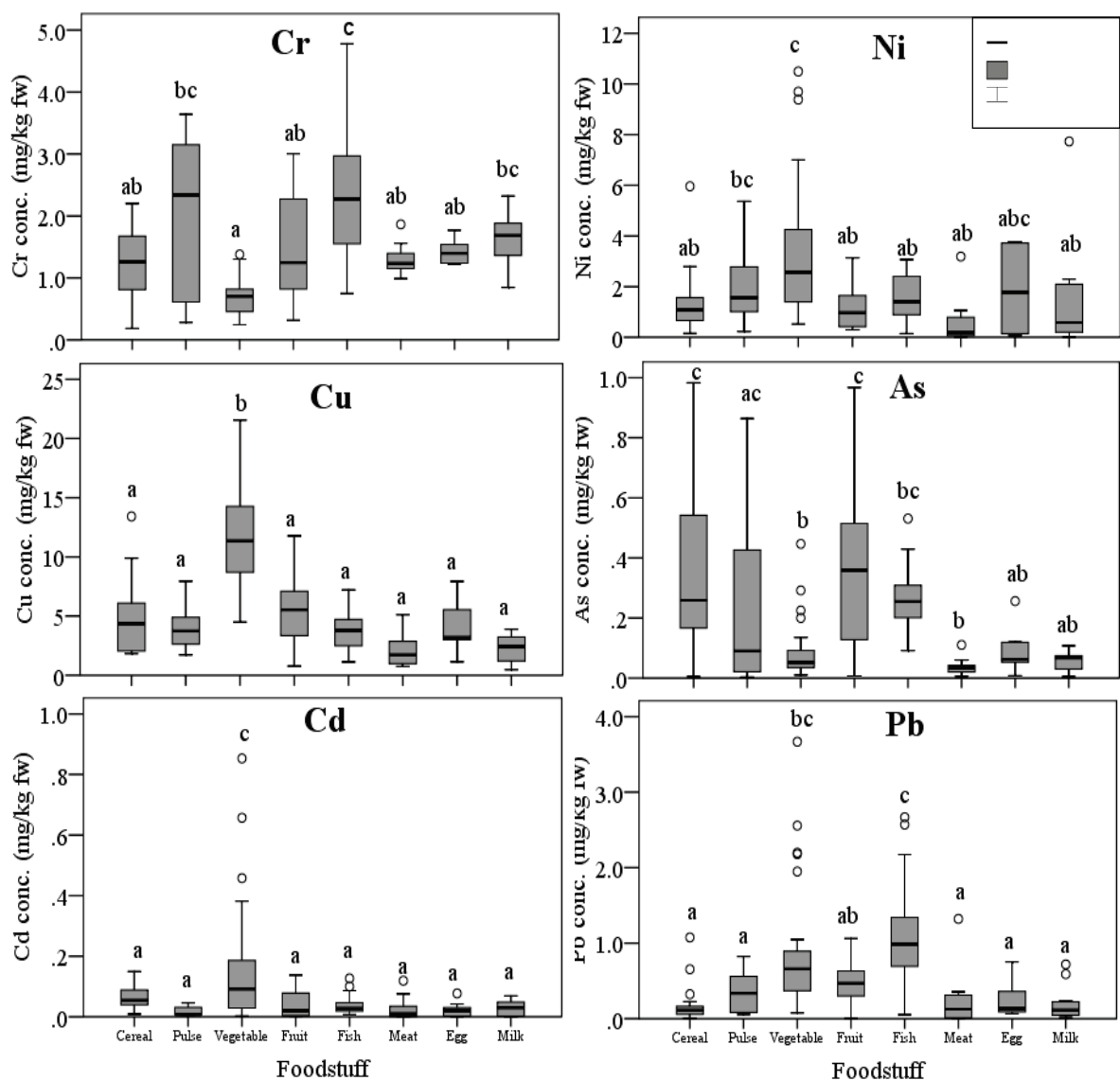
Figure 7-3. Box–whisker graphics show the distribution of trace metals in foodstuff collected from Dhaka City, Bangladesh. Circle symbols (o) represent the outlier. Different letters indicates statistical significant difference (*p < 0.05*).

The mean concentration of Cr in foodstuffs followed the descending order of fish > pulse > cereals > milk > fruit > egg > meat > vegetable. Statistical significant difference (*p < 0.05*) was observed for Cr concentrations among the food samples (**Figure 7-3**). The highest mean concentration of Cr was observed in *Banded gourami* (2.9 mg/kg) and the lowest was found in *Lagenaria siceraria* (0.60 mg/kg fw) (**Table E.1**). Chromium concentrations in most of the foods were higher than the maximum allowable total Cr in foods (**Table 7-1**), indicating severe contamination. The observed elevated concentrations of Cr in foods might be due to the application of wastewater coming from various industries such as dying and

tanning industries, photography, textile, manufacturing green varnish, paints, and inks around DEPZ, and river run-off from upstream agricultural fields (Kashem and Singh, 1999; Islam et al., 2009; Bhuiyan et al., 2011; Rahman et al., 2012; Rahman et al., 2013; Islam et al., 2014). The mean concentration of Ni in the studied foods followed the descending order of vegetable > pulse > egg > milk > fish > cereals > fruit > meat. Among the studied vegetables, the highest mean of Ni was observed in *Cucurbita maxima* (4.8 mg/kg), followed by the *Lagenaria siceraria*, *Solanum melongena* and *Solanum lycopersicum* (**Table E.1**). The concentrations of Ni in vegetables were higher than the recent study by Rahman et al. (2013) reported mean Ni concentration (1.4 mg/kg fw) in vegetables from Bangladesh.

Table 7-1. Maximum Allowable concentration (MAC) (mg/kg fw) of trace metals in foods.

Foodstuffs	Cr[b]	Ni	Cu	As[e]	Cd[e]	Pb[e]
Rice	1.0	0.5	20[b]	0.1	0.4	0.2
Maize	1.0	0.5	-	0.1	0.2	0.2
Pulses	1.0	0.5	-	0.1	0.1	0.2
Vegetables	1.0	1.5[c]	10[c]	0.1	0.05	0.1
Fruits	1.0	1.0[b]	-	0.1	0.1	0.1
Fish	1.0	0.9[a]	4.5[a]	1[a]	0.1	0.3
Meat	1.0	0.5	-	0.1	0.1	0.1
Chicken egg	1.0	-	-	0.1	0.1	0.1
Cow milk	1.0	0.1	-	0.1	0.1	0.02

[a] FAO/WHO, 2004; [b] FAO/WHO, 2002; [c] FAO/WHO, 2011; [e] JECFA, 2005

Note: MAC for Cr is total concentration.

Among the foods items, the mean Cu concentrations were followed the descending order of vegetable > fruit > egg > pulse > fish > cereals > milk > meat. The highest mean concentration of Cu was found in *Solanum melongena* (16 mg/kg) and the lowest in beef (0.10 mg/kg) (**Table E.1**). A recent study by Rahman et al. (2013) reported mean Cu concentrations of 17 and 21 mg/kg in leafy and non-leafy vegetables, respectively, collected from households in the Noakhali district in Bangladesh. Alam et al. (2003) reported Cu concentrations of 8.5 and 15 mg/kg in leafy and non-leafy vegetables, respectively, from Samta village in Bangladesh. The results showed that Cu concentration in vegetables of the present study were comparable with studies contacted for garden vegetables from the other area in Bangladesh (Rahman et al., 2013; Alam et al., 2003).

The mean As concentrations (mg/kg) were followed the descending order of cereals (0.64) > fruit (0.38) > fish (0.25) > pulse (0.24) > egg (0.087) > vegetable (0.080) > milk (0.056) > meat (0.037). The mean concentration of As in *Oryza sativa* was 0.17 mg/kg, which was in line with the previous study conducted by Williams et al. (2005) where As concentration in Bangladeshi rice was (0.13 mg/kg). The elevated As concentration in *Oryza sativa* can be due to the higher transfer of As from soil to grain in the anaerobic paddy soil systems for rice production (Williams et al., 2007; Roberts et al., 2011; Neumann et al., 2010) and uncontrolled application of As enriched fertilizers and pesticides (Renner, 2004). The second highest concentrations of As were observed in fruits (0.48, 0.41, 0.36 and 0.22 mg/kg for *Musa paradisiaca*, *Mangifera indica*, *Artocarpus heterophyllus* and *Carica papaya*, respectively) (**Table 7-1**). The mean concentration of As in cereals, fruits, fish and pulses were higher than the maximum allowable concentration (MAC) of As (0.1 mg/kg), indicating these foods are contaminated by As (**Table 7-1**). In the present study, elevated As levels in the foods can be due to the effect from both natural and anthropogenic sources, especially use of ground water for irrigation containing As (Neumann et al., 2010; Hug et al., 2011; Neumann et al., 2011), uncontrolled application of As enriched fertilizers and pesticides (Renner, 2004).

Cadmium is a metallic element that occurs naturally at low levels in the environment (Rahman et al., 2014). Food, rather than air or water, represents the major source of cadmium exposure (FSANZ, 2003). The mean Cd concentrations (mg/kg) were followed the descending order of vegetable (0.15) > cereals (0.075) > fruit (0.04) > fish (0.035) > milk (0.029) > meat (0.027) > egg (0.022) > pulse (0.018). Statistical significant difference ($p < 0.05$) was observed for Cd in vegetables with the other foods (**Figure 7-3**). Among vegetables, the highest Cd concentration was observed in *S. melongena* (mean: 0.42, range: 0.22–0.85 mg/kg) followed *S. lycopersicum*, *L. siceraria* and *C. maxima* (**Table E.1**). In the present study, concentrations of Cd in vegetables were slightly higher than some of the studies on Bangladeshi vegetables by Alam et al. (2003) (range: 0.012–0.22 mg/kg), Rahman et al. (2013) (mean: 0.13 mg/kg, range: 0.006–0.43 mg/kg) and Rahman et al. (2014) (mean: 0.14 mg/kg, range: 0.009–0.43 mg/kg). Among the foodstuffs, Cd in vegetables exceeded the MAC, indicating vegetables are contaminated by Cd.

Lead is a toxic metal that enters into the body system through air, water and food and cannot be removed by washing and cooking of foods (Sharma et al., 2007). The mean Pb concentrations (mg/kg) were followed the descending order of fish (1.0) > vegetable (0.84) > fruit (0.53) > pulse (0.35) > meat (0.25) > egg (0.24) > milk (0.20) > cereals (0.17). The highest mean concentration of Pb was found in *T. fasciata* (1.3 mg/kg) followed by *H. fossilis*

(1.1 mg/kg) and *C. punctatus* (0.63 mg/kg) (**Table E.1**). Statistically significant differences (*p < 0.05*) were observed for Pb in fish with other foods. The elevated concentration of Pb in fish and vegetables could probably due to the lead smelting activity in the study area. The concentrations of Pb in foodstuffs were higher than the recommended permissible levels in foods (**Table 7-1**), indicating severe contamination.

7.3.2 Health risk assessment

7.3.2.1 Daily intake of metals from foodstuffs

The consumption rate of foods and estimated daily intakes (EDIs) of trace metals in adult inhabitants from different food groups are listed in **Table 7-2**. To evaluate the daily intake, the median concentrations of metals in each food category were calculated and then multiplied by the respective consumption rate. Total daily intake of Cr, Ni, Cu, As, Cd and Pb were 0.97, 1.2, 5.6, 0.15, 0.047 and 0.28 mg/day, respectively (**Table 7-2**). The maximum contribution of dietary intake of metals came from rice and vegetables which is due to the highest consumption rate (445 and 191 g/person/day). Metal specific EDIs revealed that EDI of Cr, Ni, As, Cd and Pb from consumption of all examined foodstuffs were higher than the maximum tolerable daily intake (MTDI) (**Table 7-2**). Based on these insights, we conclude that Cr, Ni, As, Cd and Pb were the major component contributing to the potential health risk via consumption of the studied food items around the industrial area in Bangladesh.

The contribution of different food items to the dietary intake of trace metals are summarized in **Figure7-4**. Rice and vegetables contributed 53%, 77%, 84%, 59%, 85% and 55% for Cr, Ni, Cu, As, Cd and Pb, respectively. The dietary intake of trace metals indicated that rice and vegetables were the main sources of trace metals to diet. Rice contributed to the largest proportion (52%) of total As intake to the exposed population which can be due to the higher consumption rate than other foods. Previous studies (Ma et al., 2008; Xu et al., 2008) revealed that an elevated accumulation of arsenic in rice from arsenic enrich crop fields and excessive use of ground water as irrigation. Fish contributed 21%, 15% and 31% for Cr, As and Pb, suggested that people may exposed these metals due to the consumption of fish from the study area.

Table 7-2. Food consumption rates and estimated daily intakes of trace metals from commonly consumed foodstuff by Bangladeshi adult population.

Foodstuff	Consumption rate (g/day)	Estimated daily intake (EDI) (mg/day)					
		Cr	Ni	Cu	As	Cd	Pb
Rice	445 [a]	0.38	0.41	2.6	0.076	0.023	0.028
Maize	26.09 [b]	0.047	0.032	0.060	0.015	0.0019	0.004
Pulse	14.3 [b]	0.033	0.022	0.054	0.0013	0.0001	0.005
Vegetable	191 [c]	0.13	0.49	2.2	0.010	0.018	0.126
Fruit	50.59 [b]	0.063	0.049	0.28	0.018	0.0011	0.024
Fish	87.16 [c]	0.20	0.12	0.33	0.022	0.0024	0.086
Meat	17.4 [b]	0.021	0.0033	0.030	0.0006	0.0002	0.0022
Egg	11.3 [b]	0.016	0.020	0.036	0.0007	0.0002	0.0015
Milk	39.2 [b]	0.066	0.023	0.096	0.0026	0.0012	0.0044
Total intake from foods	882.04	0.97	1.2	5.6	0.15	0.047	0.28
Maximum tolerable daily intake (MTDI)		0.2 [d]	0.3 [e]	30 [f]	0.126 [f]	0.046 [f]	0.21 [f]

[a] Meharg et al., 2009; [b] HIES, 2011; [c] Food consumption survey of the present study; [d] RDA, 1989; [e] WHO, 1996; [f] JECFA, 2003.

The values of maximum tolerable daily intake (MTDI) represent permissible human exposure as a result of the natural occurrence of the substance in food and in drinking-water (JECFA, 2003). In the case of trace elements that are both essential nutrients and unavoidable constituents of food, a range is expressed, the lower value representing the level of essentiality and the upper value (MTDIs) which are based on various kinds of evidence: (1) studies of subjects maintained on diets containing low or deficient levels of a nutrient, followed by correction of the deficit with measured amounts of the nutrient; (2) nutrient balance studies that measure nutrient status in relation to intake; (3) biochemical measurements of tissue saturation or adequacy of molecular function in relation to nutrient intake; (4) nutrient intakes of fully breastfed infants and of apparently healthy people from their food supply; (5) epidemiological observations of nutrient status in populations in relation to intake; and (6) in some cases, extrapolation of data from animal experiments. The evaluation for the selection of MTDI also consists of combining estimated food intakes from various geographical regions with the maximum levels (MLs) of additives for the Codex General Standard on Food Additives (GSFA) (RDA, 1989; JECFA, 2003).
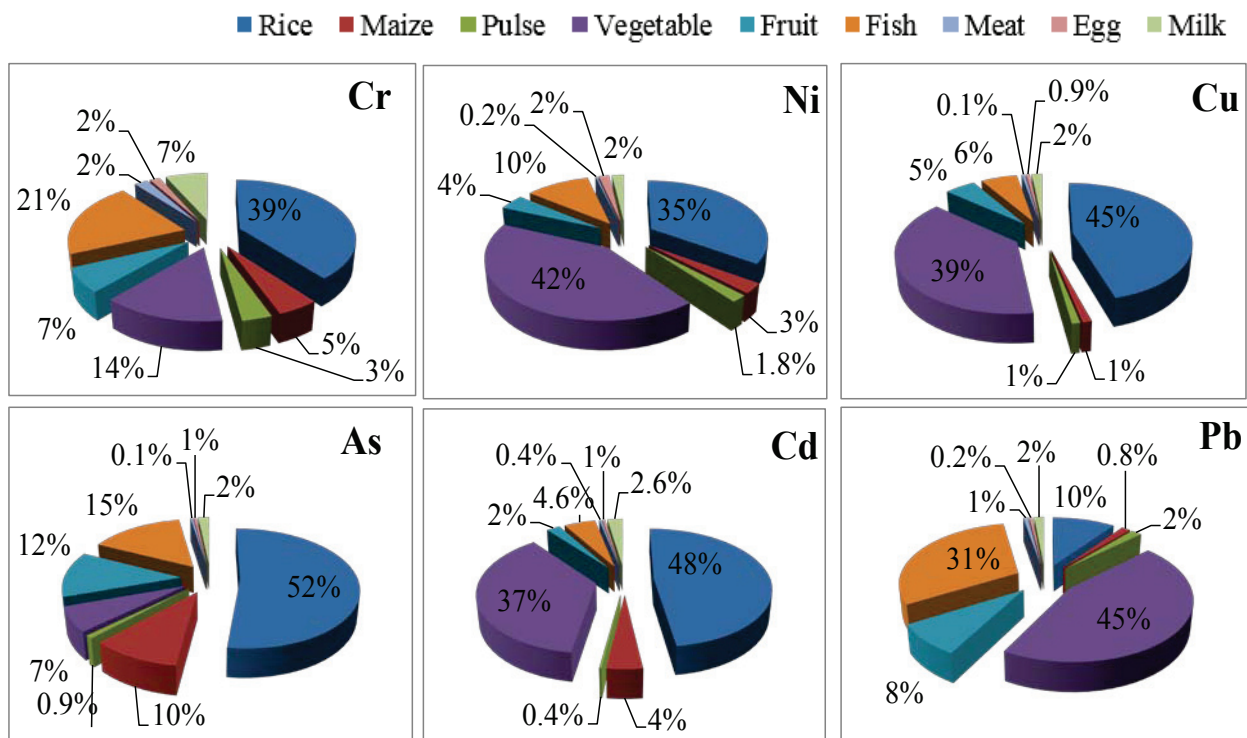
Figure 7-4. The contribution of individual food to the total daily intake of metals in the adult inhabitants around Dhaka City, Bangladesh.

7.3.2.2 Carcinogenic risk

Risk assessment is the process that evaluates the potential health effects from doses to human of one contaminant received through one or more exposure pathways. The carcinogenic health risks of As and Pb from consumption of foodstuffs by the adult inhabitants were assessed based on the target carcinogenic risk (TR). The estimated TR values of metals are shown in **Table 7-3**. The TR values were 1.7×10^{-4} for As and 2.1×10^{-7} for Pb. Carcinogenic risk of Pb from the foodstuffs was less than 10^{-6} and regarded as negligible. While, the risk for As was higher than the unacceptable level of 10^{-4}. Therefore, based on the results of the present study, the potential health risk for the local residents due to metal exposure through food ingestion should not be overlooked. Thus, the present study clearly revealed that consumption of these food items definitely pose cancer risks to the Bangladeshi population.

Table 7-3. Carcinogenic risk of As and Pb due to commonly consumed foodstuffs in Dhaka City, Bangladesh.

Target carcinogenic risk (TR)	
As	Pb
1.7×10^{-4}	2.1×10^{-7}

7.4 Conclusions

The concentrations of trace metals widely varied among foodstuffs and some metals were higher than the maximum allowable concentration (MAC) in foods. Rice contributes the highest intake of Cr, Cu, As, and Cd, whereas vegetables contributes for Ni and Pb. Most of the metals from dietary intake were higher than the MTDI, indicated that people would experience significant risks if they ingest metals from these food items. Human health risks associated with food consumption were not negligible, and the sources of metal pollution in foodstuffs should be controlled. Furthermore, this study recommended that an urgent attention is required to evaluate the trace metal concentrations in human beings and animals of the study area in order to evaluate if any potential health risks from trace metal exposure.

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Chapter 8

GENERAL DISCUSSION, CONCLUSIONS AND
RECOMMENDATIONS

General Discussion, Conclusions and Recommendations

8.1 Discussion

This study examined trace metal contaminations from different environmental media around Dhaka City in wide-scale monitoring campaigns in Bangladesh. The study offered us the opportunity to observe the present situation of trace metal contamination. We also gained relevant information regarding the major contributors for the release of these pollutants in the environment of the study area. By carrying out this study, we also obtained the situation of health risk due to metal exposure through ingestion, dermal contact and inhalation pathways.

8.1.1 Metal concentrations in water and sediment

A wide range of values for metal concentrations in sediments were observed among the sampling sites. Factors such as salinity, geomorphological setup, and land runoff might have played a role in the variation of metals. It was observed that the highest Cr concentration in both water and sediment at B1 site is presented in **Figures 3-2, 3-3** and **3-4**, which can be due to the effects from tannery and dyeing industries of this site. The main leather tanning zone with about 270 tanneries were situated on the banks of Buriganga River on an area of 4 km^2 of site B1. The discharge of waste from tanneries was most probably responsible for the high Cr in sediment at B1 site (Ahmad et al., 2010, Mohiuddin et al., 2011). Slightly higher concentration of Cd in water and sediments was observed at B3 site (**Figures 3-2, 3-3** and **3-4**) which can be due to the presence of metal processing, battery factories and paint industries at this site (Caruso and Bishop, 2009). It was understandable that trace metals in water and sediment samples were higher in winter than summer season. The lower levels of trace metals in water during summer might be due to rainfall effects which could increase the lixiviation process and contribute to the dilution of trace metals during the wet season (Khattabi et al., 2007). On the other hand, metals in sediment during winter season were slightly higher than summer which can be attributed to the variation in water capacity of the river, where water input in river is generally limited during winter, resulting in the precipitation of pollutants in the sediment. Among the studied metals, elevated Pb was observed in sediment (1846, 1756 mg/kg dw during winter and summer season) (**Figure 3-4**), which can be attributed to a nearby Pb smelting factory. In sediment, Pb concentrations in most of the sites were slightly higher in winter compared to summer which indicates that there could be some changes in

organic profile due to resuspension/deposition of sediment or by changes in redox and pH conditions (Liang and Wong, 2003; El Nemr et al., 2007; Bastami et al., 2012). The mean concentrations of all the analyzed trace metals were higher than those of the toxicity reference values, lowest effect levels and severe effect level (**Table 3-5**), indicating severe pollution of sediment by trace metals. Metals in sediment of the rivers around Dhaka City were higher than the reference site (Bogra district, Bangladesh) **(Table 8-1)**, indicating the input of metals due to the industrial and other anthropogenic interventions.

The sequential extraction indicated that the residual fraction dominated the Cr (56%), Ni (48%), As (56%) and Pb (34%) during winter and Cr (50%), Ni (43%), As (53%) and Pb (31%) during summer season, respectively (**Figure 4-2**) suggesting the strongest associations to the crystalline sedimentary components of these metals (Hamilton et al., 1984). According to the partitioning pattern, a considerable proportion of Cd (26% during winter and 25% during summer) was associated with exchangeable fraction (**Figure 4-2**) and can be more available to aquatic life. From **Figure 4-2**, the geochemical fractionation results showed some variations among the defined chemical fractions for the same metal or in different metals which can be attributed by numerous factors, such as weathering, mineral transport, anthropogenic inputs, and physicochemical components of sediments (Sundaray et al., 2011). Fe–Mn oxides and organic matter plays excellent scavengers role for the removal of trace metals from the water column in the aquatic environments (Dhanakumar et al., 2013). Fe–Mn oxy-hydroxide was the scavenger for Ni, As and Pb (**Figure 4-2**), which can be attributed to the adsorption, flocculation and co-precipitation of trace metals with the colloids of Fe and Mn oxy-hydroxide (Rath et al., 2009).

8.1.2 *Metal concentrations in soil*

The level of trace metals varied among the sampling sites of different land-use types and followed the descending order of TW > MW > EW > AF > GW > BS > CW > BF > HW > GPS > PG > PA. The highest mean concentration of Cr was obtained at the tannery waste disposal site (1112 mg/kg) (**Figure 5-2**), which can be due to the waste from chromate smelters (Srinivasa et al., 2010). The elevated mean concentrations of Ni (749 and 525 mg/kg) and Cu (457 and 553 mg/kg) were observed in soil at MW and EW disposal site (**Figure 5-2**) that can be attributed due to the emission from metal smelters. Such extremely high levels of Ni and Cu in soils can be found in metal industries and waste disposal sites, resulted from localized additions or accidental spillages of highly concentrated materials, uncontrolled

industrial and waste burning activities (Krishna and Govil, 2007; Srinivasa et al., 2010). Among the land-use types, TW, BF, BS and AF sites showed a considerable level of As (**Figure 5-2**). Interestingly, TW site showed the highest As concentration (112 mg/kg) which can be due to the excessive use of chemicals especially arsenic sulfide (Bhuiyan et al., 2011). Moreover, emission and waste from brick fields and incineration activities might contribute the high concentration of As (Olawoyin et al., 2012). Arsenic in agricultural soils can be derived from both natural and anthropogenic sources, especially use of ground water for irrigation (Neumann et al., 2011), uncontrolled application of As enriched fertilizers and pesticides (Renner, 2004). The elevated concentration of Cd was obtained from the EW, MW, TW and BF sites that can be attributed due to the metal processing, battery manufacturing and smelting industries. Severe Cd pollution has been reported from areas surrounding smelters in many countries (Martley et al., 2004). MW, EW and BS sites showed the elevated concentrations of Pb which can be due to the emission of Pb contaminated waste from these sites (Srinivasa et al., 2010). **Figure 5-2** showed higher standard deviation for metals in soil, and such high deviation may be indicative of the lack of uniformity of the elemental distribution among the sites. This was probably due to various land use activities and disturbances such as digging, excavation, and construction, as well as other natural processes such as weathering and erosion, which could alter stabilization of the soil environment (Amuno, 2013).

Site specific concentrations of trace metals mostly exceeded the Dutch soil quality target and intervention values (**Figure 5-2**), indicated that soils might be seriously affected by trace metals and could potentially cause adverse effect on humans, plants and animals (Man et al., 2010). Geochemical fractionation of soil indicated that Cr, Ni, Cu, As, Cd and Pb were predominantly associated with the residual fraction followed by the organically bound phases (**Figure 6-3**). The average percentage of Cu in soil (agriculture fields) for exchangeable and carbonate bound fractions were slightly higher than other metals, implying that Cu is more mobile and phyto-available.

Table 8-1. Comparison of metal concentrations in the environmental media of Dhaka City with the reference site (Bogra district) of Bangladesh.

Metals	Soil (mg/kg dw)		Sediment (mg/kg dw)		Water (µg/L)	
	Dhaka	Ref. site	Dhaka	Ref. site	Dhaka	Ref. site
Cr	384	44	695	109	27	7.7
Ni	192	62	355	95	19	3.7
Cu	312	37	191	76	16	6.7
As	64	35	35	25	15	4.3
Cd	7.1	2.5	18	1.2	0.26	0.05
Pb	199	59	356	58	4.1	0.91

8.1.3 Metal concentrations in foodstuffs

For all types of foods, relatively large variability in metal concentrations was observed, even within the same kind of food. The variation in metal concentrations in foodstuffs could be due to variation in absorption and accumulation capabilities, growth period and stages of food crops and physiographic differences among the study areas (Saha and Zaman, 2013; Santos et al., 2004). In this study three commonly consumed available fish species were considered for trace metal analysis and metals were varied considerably among the species which can be due to the ingestion behavior from different layer of aquatic environment. Cr, Ni, As and Pb in most of the food samples were higher than the maximum tolerable limits in foods, indicated that the foods were contaminated by these metals. Estimated daily intakes (EDIs) of Cr, Ni, As, Cd and Pb from consumption of all examined foodstuffs were higher than the maximum tolerable daily intake (MTDI) (**Table 7-2**), indicated that these metals would create potential health risk via consumption of foods around the industrial area in Dhaka City, Bangladesh. The contribution of different food items to the dietary intake of trace metals are presented in **Figure7-4** indicating the main sources of trace metals from rice, vegetables and fish.

8.1.4 Integrated risk assessment

In recent years, there has been an increasing risks from industrial hazardous chemicals which impact on human health. It is quite difficult to minimize the risk within single approach. So, it is suggested to implement the integrated risk assessment. In this chapter, integrated risk assessment highlights the assessment of risks from continuous emissions of trace metals into soil, water and foods through the unplanned industrial, commercial and urban activities. The risk assessment is carried out to estimate the trace metals and their magnitude of exposure

through three exposure media (foods, soil and water). The estimated daily intakes (EDIs) of trace metals in adult inhabitants are listed in **Table 8-2**. It was found that EDI of Cr, Ni, As, Cd and Pb from three exposure media exceed the value of the maximum tolerable daily intake (MTDI) (**Table 8-2**). Based on these results, we conclude that Cr, Ni, As, Cd and Pb were the major component contributing to the potential health risk through the integration of three exposure media around the industrial area of Dhaka City, Bangladesh.

Table 8-2. Intake of metals (mg/day) from three different exposure media.

Exposure media	Estimated daily intake (EDI) (mg/day)					
	Cr	Ni	Cu	As	Cd	Pb
Metal intake from foods	0.97	1.2	5.6	0.15	0.047	0.28
Metal intake from soil	0.024	0.021	0.027	0.006	0.002	0.019
Metal intake from water	0.11	0.075	0.066	0.060	0.001	0.016
Total intake from three media	1.1	1.3	5.7	0.22	0.05	0.32
Maximum tolerable daily intake (MTDI)	0.2 [d]	0.3 [e]	30 [f]	0.126 [f]	0.046 [f]	0.21 [f]

[d] RDA, 1989; [e] WHO, 1996; [f] JECFA, 2003.

8.2 Summary of Findings

The first part of the thesis addressed the levels of trace metals in water and sediment collected at nine sites of three rivers around Dhaka City (Turag, Buriganga and Shitalakha) with the assessment of water and sediment quality. The second part also described the levels of the same pollutants in sediment and fish, with the assessment of chemical speciation and metals bioaccumulation in fish species. The third component described the levels of metals in soils of different land uses and their transfer to the vegetables species and last part of the thesis discussed about the concentration of trace metals in various foodstuffs with the implication to public health. Given below are summary of the findings from the five individual chapters that seek to provide information addressing environmental problems based on trace metal contamination in the environmental media around the capital city, Bangladesh.

8.2.1 Assessment of trace metal contamination in water and sediment of some rivers in Bangladesh

- Total concentrations of Cr, As and Pb in water were higher than the World Health Organization prescribed values for drinking water quality guidelines which raised concern of health risks.
- Trace metals exerted distinct seasonal variation with higher concentrations in winter season.
- Elevated levels of Cr and Pb were mainly derived from untreated waste from tanneries, lead smelting factory and battery manufacturing industries.
- Metals in sediment exceeded the toxicity reference values indicating severe metal pollution.

8.2.2 Chemical speciation of trace metals in sediment and their bioaccumulation in fish on three urban rivers, Bangladesh

- Geochemical fractionation procedure indicated that Cr, Ni, As and Pb were predominately associated with the residual fraction.
- In comparison with the other studies that were conducted near the industrial area indicated that fishes were contaminated by trace metals.
- Sediment ingestion as well as omnivore feeding behavior affects higher metal accumulation in *T. fasciata.*
- Among the fish species investigated, *T. fasciata* can be used as a potential bio-indicator for the contamination of trace metals in those riverine environments.

8.2.3 Trace metal concentrations in different land-use soils in the capital city of Bangladesh and health risk assessment

- Elevated levels of trace metals were observed in soils of agriculture field (AF), metal workshop (MW), tannery waste disposal (TW), Electric waste (EW) and Waste burning site (BS) sites which caused potential risks.
- Site specific concentrations of trace metals in soil mostly exceeded the Dutch soil quality target and intervention values, indicating severe metal pollution.

- Target populations of the study area were mostly exposed to trace metals through the ingestion exposure pathway.

- Carcinogenic risks of As were within the acceptable range of 10^{-6} to 10^{-4} for all the site, those for some sites such as TW were relatively close to the unacceptable level of 10^{-4}.

8.2.4 Trace metal contamination in agricultural soil and vegetables around the industrial area of Dhaka City, Bangladesh

- Significant amount of trace metals were found in soils of Buriganga riverside agricultural fields due to intensive uncontrolled operation of various industries.

- In soil, metals were predominantly associated with the residual fraction followed by the organically bound phase which is believed to hold metals within the crystalline structure of primary and secondary minerals.

- Higher metal transfer factor (TF) was observed for Cu and Pb where coefficient of variation was minimal among the TFs calculated using different extraction fraction, whereas any TFs did not perform well for the other metals.

- It is concluded that either fractionation is not a good indicator of bioavailability or air, not soil, may be a major pathway for the metal transfer to vegetables.

8.2.5 Monitoring of trace metals in foodstuffs grown around the industrial area of Dhaka City, Bangladesh and health risk assessment

- Comparatively higher metals were found in vegetables and fish.

- Cr, Ni, As and Pb were higher than the maximum tolerable limits in most of the foods.

- Among the studied food items, rice, vegetables, fruit and fish were the major contributors for metal intake.

- The daily intake of metals from three exposure media (food, soil and water) were higher than maximum tolerable daily intake (MTDI) indicated that local residents might pose significant health risk.

8.3   Conclusions

My research work emphasized on the concentration, contamination and bioaccumulation of trace metals (Cr, Ni, Cu, As, Cd and Pb) in the urban environment especially around Dhaka

City, Bangladesh. A wide-scale monitoring of these pollutants was undertaken by multidimensional approaches. The purposes of the studies were to understand the recent environmental state of trace metals associated with health risks. The environmental media such as water, sediment, soil and foodstuffs (e.g. rice, vegetables and fish) were noted to be severely polluted where the levels of metals were higher than the international guidelines. The existing sources of trace metals primarily were emanated by the intensive uncontrolled operation of various industrial, commercial and urban activities. However, it is well established that the trace metals especially As, Cd and Pb were the most concern for the health risk of that urban people.

8.4   Recommendations for further research

One of the highlights in this study with respect to the analysis of trace metals in the environmental media and foodstuffs from three riverine urban ecosystems around Dhaka City, Bangladesh was the recurrence of relatively elevated levels. It is of interest to fully resolve the metal contaminations.

Among the sites studied, the levels of contamination from trace metals were much elevated in the environment having untreated waste from metal workshop, tanneries, e-waste, incinerations and other activities. Given present hypothesis that untreated waste from different industries may be contributing to contemporary emissions of trace metals, especially in developing countries like Bangladesh, it is important to undertake further studies to help quantify the extent of impact from these activities. Assessing this critically, would help us understand and tackle the relatively high levels of trace metals in the other urbanized area in Bangladesh.

In recognition of the environmental problems of trace metals the study identified, a precautionary approach to mitigate the problems based on risk management is advanced through the following recommendations:

(I)   Sensitization on the need to refrain from waste burning; relocation of industrial and municipal solid waste disposal sites away from residential areas.

(II)   Polluted sediments from the river bed should be removed and dumped to an isolated area, application of industrial waste and polluted sediments to the nearby agricultural fields should be stopped.

(III)   The species of vegetables that uptake lower metals should be selected for cultivation and grafting technology should be used especially for *solanum melogena*.

(IV)   The present work in Bangladesh was the first attempt for the intensive monitoring of trace metals in the urban ecosystems. It will be important to expand such monitoring on the trace metals concentrations in human beings (blood and urine) and animals of the study area.

(V)   Government should have to take effective measures in relation to the proper scientific assessment by the scientists and researchers regarding the monitoring and the impact of human activities on metal pollution in this area.

(VI)   Finally, developing countries like Bangladesh, should adopt ecofriendly and economically feasible technology from developed countries for the treatment of industrial waste to control the metal pollution.

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2. **Md Saiful Islam** and Shigeki Masunaga. Monitoring of heavy metals in industrial waste water of Dhaka urban area, Bangladesh. *The International Conference on Storm water and Urban Water Systems Modeling, The Marriott Courtyard Toronto Brampton, Toronto, Canada*. (26-27 February, 2014).
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APPENDIX

Supplementary Information

APPENDIX A
Supplementary Information for Chapter 3

Table A.1. Total metal concentration (µg/L) in water of three rivers around Dhaka City, Bangladesh.

Sites	Cr		Ni		Cu		As		Cd		Pb	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
T1	11	6.0	13	17	12	8.3	12	7.7	0.30	0.23	3.7	2.7
T2	16	8.7	19	24	20	12	19	11	0.29	0.25	4.5	3.1
T3	15	9.8	16	21	42	10	19	12	0.21	0.20	3.7	3.1
B1	96	82	16	18	23	8.8	24	16	0.35	0.28	6.3	5.2
B2	60	46	14	18	22	8.9	24	16	0.34	0.31	9.5	6.8
B3	56	40	26	40	22	20	16	11	0.41	0.34	3.8	2.6
S1	6.8	5.0	13	17	14	8.3	19	9.8	0.22	0.18	3.7	2.7
S2	8.0	5.5	13	19	22	10	17	9.2	0.21	0.16	3.3	2.4
S3	9.8	7.5	14	23	22	11	17	8.2	0.27	0.20	3.7	3.0

Table A.2. Dissolved metal concentration (µg/L) in water of three rivers around Dhaka City, Bangladesh.

Sites	Cr		Ni		Cu		As		Cd		Pb	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
T1	2.4	1.3	2.8	1.8	1.6	3.2	2.3	0.96	0.006	0.005	0.77	0.86
T2	3.5	1.9	4.0	2.3	16	4.0	4.8	1.1	0.006	0.006	0.94	1.3
T3	3.2	1.2	3.4	1.6	7.4	2.8	6.2	1.0	0.004	0.004	0.74	0.90
B1	21	2.1	3.4	3.0	3.3	4.4	4.8	1.3	0.004	0.005	1.3	1.2
B2	13	2.6	3.0	1.8	1.5	3.2	4.7	1.2	0.003	0.006	0.65	1.0
B3	12	2.5	5.5	1.6	9.1	2.6	3.3	1.3	0.004	0.009	0.76	1.7
S1	1.5	2.7	2.8	3.3	1.9	4.6	3.7	1.2	0.004	0.005	0.77	1.6
S2	1.8	0.54	2.7	1.8	3.5	1.9	3.4	1.6	0.004	0.003	0.71	0.40
S3	2.3	2.1	3.1	2.8	3.1	5.7	3.4	1.2	0.003	0.005	0.76	1.3

Table A.3. Metal concentration in sediment sample [mg/kg dry weight (dw)] of three rivers around Dhaka City, Bangladesh.

Sites	Cr		Ni		Cu		As		Cd		Pb	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
T1	395	112	242	139	187	65	40	12	14	8.4	70	45
T2	658	300	362	187	254	102	41	23	16	13	141	66
T3	937	318	493	232	302	121	34	15	15	11	133	81
B1	2471	2039	375	365	404	204	50	41	19	18	159	90
B2	908	563	361	314	339	176	47	35	20	23	1846	1756
B3	652	617	606	522	304	192	58	46	29	26	574	576
S1	578	406	418	392	165	89	33	27	18	12	176	148
S2	429	214	376	198	127	76	39	16	24	21	170	81
S3	566	352	466	334	180	146	39	28	16	12	192	100

APPENDIX B
Supplementary Information for Chapter 4

Table B.1. Measured and certified values of heavy metal concentration [mg/kg dry weight (dw)] in standard reference material of NMIJ CRM 7303-a lake sediment and DORM-2 – dogfish muscle.

Metal	NMIJ CRM 7303-a lake sediment			DORM-2 – dogfish muscle		
	Certified value	Measured value (n=3)	Recovery (%)	Certified value	Measured value (n=3)	Recovery (%)
Cr	39.1±2.8	39.2±0.2	100	34.7±5.5	33.9±2.2	98
Ni	21.8±2.5	21.6±0.4	99	19.4±3.1	19.1±1.1	98
Cu	23.1±3.1	23.3±0.6	101	2.34±0.16	2.52±0.10	108
As	8.6±1.0	8.5±0.1	99	18±1.1	17.7±1.6	98
Cd	0.342±0.017	0.341±0.010	100	0.043 ± 0.008	0.044±0.004	102
Pb	31.3±1.1	31.7±0.3	101	0.065 ± 0.007	0.068±0.005	105

Table B.2. Metal concentration in fish species [mg/kg wet weight (ww)] of three rivers in Bangladesh (n=3).

Sites	Species		Cr Winter	Cr Summer	Ni Winter	Ni Summer	Cu Winter	Cu Summer	As Winter	As Summer	Cd Winter	Cd Summer	Pb Winter	Pb Summer
Turag	*C. punctatus*	Mean±SD	2.5±0.55a	1.3±0.29a	0.44±0.08a	0.18±0.04a	1.9±0.35a	1.2±0.08a	0.25±0.02a	0.093±0.002a	0.011±0.003a	0.008±0.000a	0.63±0.12a	0.13±0.11a
		Range	1.9-2.9	1.0-1.6	0.37-0.53	0.14-0.22	1.5-2.2	1.1-1.3	0.24-0.28	0.091-0.094	0.008-0.013	0.007-0.008	0.49-0.72	0.052-0.26
	H. fossilis	Mean±SD	2.4±0.25a	1.5±0.05a	1.1±0.16b	0.91±0.10b	5.1±0.67b	3.4±0.41b	0.28±0.02a	0.14±0.008ab	0.026±0.004b	0.024±0.001c	1.3±0.08b	0.65±0.14ab
		Range	2.2-2.7	1.5-1.6	0.99-1.3	0.80-1.0	4.4-5.7	3.1-3.9	0.27-0.30	0.13-0.15	0.023-0.03	0.023-0.025	1.2-1.4	0.53-0.80
	T. fasciata	Mean±SD	2.9±0.67a	2.3±0.08b	2.5±0.20c	2.3±0.23c	3.7±0.38c	2.2±0.27c	0.29±0.11a	0.28±0.12b	0.015±0.002a	0.025±0.006c	1.5±0.05c	0.85±0.41b
		Range	2.3-3.6	2.2-2.4	2.3-2.7	2.1-2.6	3.3-4.0	1.9-2.5	0.22-0.41	0.20-0.42	0.014-0.018	0.019-0.030	1.5-1.6	0.41-1.2
Buriganga	*C. punctatus*	Mean±SD	3.5±0.47ab	1.4±0.39a	2.9±0.02a	1.5±0.26a	5.5±0.35ab	2.7±0.69a	0.30±0.03ab	0.092±0.001a	0.025±0.002a	0.044±0.014a	1.4±0.16a	0.81±0.02a
		Range	3.1-4.0	1.0-1.8	2.8-2.9	1.3-1.8	5.2-5.9	2.3-3.5	0.26-0.32	0.091-0.092	0.022-0.026	0.028-0.053	1.2-1.5	0.78-0.83
	H. fossilis	Mean±SD	2.8±0.93a	2.1±0.44ab	3.0±0.018bc	1.6±0.29a	6.0±1.1a	4.4±0.41b	0.34±0.04a	0.24±0.019ab	0.034±0.01a	0.053±0.000a	1.4±0.10ab	1.0±0.07ab
		Range	1.8-3.6	1.6-2.5	2.9-3.0	1.3-1.9	5.2-7.2	4.2-4.9	0.32-0.39	0.23-0.26	0.026-0.045	0.052-0.53	1.3-1.5	0.91-1.0
	T. fasciata	Mean±SD	4.5±0.24b	2.5±0.38b	3.0±0.04c	2.4±0.12b	4.1±0.56b	4.1±0.50ab	0.28±0.01b	0.36±0.14b	0.049±0.018a	0.095±0.034a	2.5±0.26c	1.2±0.18b
		Range	4.3-4.8	2.3-3.0	3.0-3.1	2.3-2.5	3.5-4.5	3.7-4.7	0.27-0.28	0.28-0.53	0.033-0.068	0.060-0.13	2.2-2.7	1.0-1.3
Shitalakha	*C. punctatus*	Mean±SD	2.3±0.26a	1.1±0.11a	0.69±0.28a	0.55±0.29a	4.2±0.5a	2.5±0.5a	0.28±0.05a	0.12±0.005a	0.036±0.009a	0.031±0.009a	0.64±0.26a	0.16±0.04a
		Range	2.1-2.6	1.0-1.2	0.40-0.95	0.29-0.86	3.8-4.7	2.3-3.1	0.23-0.33	0.12-0.13	0.026-0.043	0.020-0.038	0.35-0.79	0.13-0.20
	H. fossilis	Mean±SD	2.9±0.64ab	1.1±0.38a	1.5±0.12ab	0.94±0.06a	5.8±0.20b	3.6±0.44a	0.37±0.07a	0.22±0.01bc	0.024±0.01ab	0.040±0.01ab	1.2±0.29a	1.0±0.14bc
		Range	2.4-3.6	0.75-1.5	1.4-1.6	0.89-1.0	5.7-6.0	3.1-3.9	0.29-0.43	0.21-0.22	0.011-0.034	0.029-0.051	0.85-1.4	0.88-1.1
	T. fasciata	Mean±SD	3.6±0.42b	1.4±0.42a	1.8±0.67b	1.4±0.53a	3.0±0.48c	3.8±1.4a	0.37±0.04a	0.22±0.03c	0.014±0.002b	0.071±0.019b	1.3±0.36a	0.69±0.29c
		Range	3.2-4.0	1.1-1.9	1.1-2.4	0.85-1.9	2.5-3.4	2.3-5.0	0.34-0.41	0.20-0.25	0.012-0.016	0.049-0.086	1.1-1.7	0.40-1.0

Vertically, letters a, b and c show statistically significant differences (p < 0.05) among the fish species of each river.

Table B.3. Comparison of trace metal concentration [mg/kg wet weight (ww)] in fish muscle with the reported values in the literatures.

Study area	Cr	Ni	Cu	As	Cd	Pb	References
Turag River (Bangladesh)	2.2 (0.97-3.6)	1.2 (0.14-2.7)	2.9 (1.1-5.7)	0.22 (0.091-0.42)	0.018 (0.008-0.03)	0.84 (0.052-1.6)	This study
Buriganga River (Bangladesh)	2.8 (1.0-4.8)	2.4 (1.3-3.1)	4.5 (2.3-7.2)	0.27 (0.091-0.53)	0.05 (0.022-0.13)	1.4 (0.78-2.7)	This study
Shitalakha River (Bangladesh)	2.1 (0.75-4.0)	1.1 (0.29-2.4)	3.8 (2.3-6.0)	0.26 (0.12-0.43)	0.036 (0.011-0.086)	0.83 (0.13-1.7)	This study
Bangshi River (Bangladesh)	0.098-0.43	0.14-0.91	1.7-9.0	0.41-1.3	0.019-0.18	0.37-2.1	Rahman et al. (2012)
Rivers (Bangladesh)	NA	0.80 (0.39-2.0)	1.7 (0.49-7.7)	NA	0.029 (0.013-0.042)	0.88 (0.096-3.3)	Sharif et al. (1993)
Neretva river (Bosnia and Herzegovina)	NA	NA	0.068–16.059	NA	0.013–0.055	0.055–0.703	Djedjibegovic et al. (2012)
Calicut fresh water (India)	0.73	0.11	0.59	NA	0.04	0.13	Sankar et al. (2006)
Daniester river (Eastern Europe)	0.038-0.06	3.13-2.7	1.8-3.13	NA	0.038-0.04	1.85-3.17	Sapozhnikova et al. (2005)
Savannah river (South Carolina)	0.330	NA	0.36	0.09	0.01	0.03	Burger et al. (2002)

Note: NA = data not available

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APPENDIX C

Supplementary Information for Chapter 5

Table C.1. Descriptions of different assorted land uses and their respective number of sites under present investigation.

Types of land use	Category	Number of sites	Description about the sampling sites
Agriculture field (AF)	Agriculture	9	Traditional farming systems, grown different types of vegetables and cereal crops with chemical fertilizers and pesticides.
Park area (PA)	Recreational	5	The area for exercise and other recreation for the people which also surrounded by some industries.
Playground (PG)	Recreational	4	The field for play for adults and other residents.
Petrol station (PS)	Commercial	4	Gas and petrol filling station, dispose of some waste from the car around the station.
Metal workshop (MW)	Industrial	6	Recycling of toxic metals with some machinery activities, metal smelting and preparing new products.
Brick field (BF)	Industrial	6	Brick kiln field, burning of coal and wood for making bricks.
Household waste (HW)	Waste dump	5	Disposal site of the mixture of house hold waste from the city.
Garments waste (GW)	Waste dump	6	Disposal site of the garments waste with small cloths, polybag and dyeing materials.
Electric waste (EW)	Waste dump	5	Non-recyclable electric waste dumping site, breaking down of electronic components such as computers, refrigerators and printers on the land.
Tannery waste (TW)	Waste dump	8	Disposal site of tannery waste with leather products and cadmium, chromium and arsenic are used for leather processing.
Construction waste (CW)	Waste dump	6	Field for demolishing building materials, wood, scrap metal, concrete and bamboo etc.
Waste burning site (BS)	Waste incineration	6	Sites for the burning of house hold waste, farm waste and mixture of industrial waste.

Table C.2. Some toxicological characteristics of the investigated trace metals used for health risk assessments for the present study.

Toxicological parameters	unit	Cr	Ni	Cu	As	Cd	Pb	References
$RfD_{ingestion}$	mg/kg/day	0.003	0.02	0.04	0.0003	0.001	0.004	USDOE, 2011
$RfD_{dermal\ contact}$	mg/kg/day	0.003	0.02	0.04	0.0003	0.001	0.004	USDOE, 2011
$RfD_{inhalation}$	mg/kg/day	0.0001	0.00009	0.005[a]	0.000015	0.00001	0.0005[a]	USEPA, 2010
$CSF_{ingestion}$	$(mg/kg/day)^{-1}$				1.5		0.0085[a]	USEPA, 2010
IUR	$(\mu g/m^3)^{-1}$				0.0043		0.000012	USDOE, 2011
ABS_{GI}					0.41		1	USEPA, 2011

[a]USDOE, 2011
RfD = Reference dose
CSF = Chronic oral slope factor
IUR = Chronic inhalation unit risk
ABSGI = Gastrointestinal absorption factor

Table C.3. Metal concentration (mg/kg) in soils of different land uses and guidelines value.

Sites		Cr	Ni	Cu	As	Cd	Pb	References
Agriculture field (n=9)	Mean±SD	384±297[a]	192±108[a]	311±129[abc]	64±19a[b]	7.1±2.6[a]	199±147[ab]	
	Range	166-1120	113-443	165-510	41-90	4.2-12	89-567	
Park area (n=5)	Mean±SD	37±24[b]	25±11[a]	46±32[a]	19±7.8[a]	6.9±4.8[ab]	92±56[ab]	
	Range	6.3-58	8.3-37	10-92	12-31	2.0-14	21-170	
Playground (n=4)	Mean±SD	20±17[b]	117±28[a]	82±53[ac]	18±6.3[a]	3.5±1.0[ab]	49±38[ab]	
	Range	2.4-39	89-143	46-161	10-24	2.0-4.2	13-100	
Petrol station (n=4)	Mean±SD	42±26[b]	105±113[a]	134±87[abc]	20±4.1[a]	10±6.3[ab]	62±32[ab]	
	Range	17-73	37-273	36-220	16-24	5.0-19	40-108	
Metal workshop (n=6)	Mean±SD	91±45[ab]	749±312[b]	457±225[bc]	58±20[ab]	27±20[ab]	346±256[ab]	
	Range	31-134	313-1044	156-823	31-85	7.6-52	124-806	
Brick field (n=6)	Mean±SD	75±39[b]	99±49[a]	131±115[ac]	77±33[ab]	20±9.3[ab]	174±87[ab]	
	Range	40-137	35-183	27-333	34-123	5.4-30	52-281	This study
Household waste (n=5)	Mean±SD	71±40[b]	49±42[a]	99±74[ac]	36±5.7[a]	11±3.4[ab]	139±54[ab]	
	Range	29-135	21-121	37-217	29-44	6.3-13	64-201	
Garments waste (n=6)	Mean±SD	164±131[ab]	126±56[a]	282±303[abc]	56±38[ab]	13±13[ab]	250±84[ab]	
	Range	30-395	34-207	31-728	8.7-116	1.8-33	170-362	
Electric waste (n=5)	Mean±SD	140±112[ab]	525±255[b]	553±217[b]	67±34[ab]	34±31[b]	350±282[ab]	
	Range	54-333	315-923	175-701	24-103	5.2-80	148-842	
Tannery waste (n=8)	Mean±SD	1112±133[c]	144±87[a]	303±253[abc]	112±88[b]	27±20[ab]	87±63[a]	
	Range	861-1258	52-283	29-780	23-277	11-74	21-178	
Construction waste (n=6)	Mean±SD	34±15[b]	181±187[a]	278±244[abc]	42±26[a]	9.0±8.3[ab]	162±75[ab]	
	Range	12-35	34-517	20-589	15-84	4.0-26	93-283	

Waste burning site (n=6)	Mean±SD	120±59[b]	120±44[a]	366±182[abc]	68±21[ab]	14±5.6[ab]	365±219[b]	
	Range	52-196	49-155	152-608	33-93	5.3-22	145-706	
Dutch soil quality standard (Target Value)		100	35	36	29	0.8	85	VROM, 2000
Dutch soil quality standard (Intervention Value)		380	210	190	55	12	530	VROM, 2000
Canadian Environmental Quality Guidelines		64	50	63	12	1.4	375	CCME, 2003
China Environmental Quality Guidelines (Grade II: Agricultural and relate use)		300	NA	200	30	0.6	70	SEPA, 1995
Department of Environmental Protection, Australia		50	60	60	20	3	300	DEP, 2003
Australian Guideline on the Investigation Levels for Soil (Residential with garden)		NA	NA	1000	100	20	300	NEPC, 1999
Sweden Soil Remediation Goals (Most sensitive type of land use)		NA	NA	100	15	0.4	80	SEPA, 2002

Note: Vertically different letters indicate statistically significant ($p < 0.05$).

Table C.4. Hazard Quotients (*HQs*) of trace metals due to ingestion, dermal contact and inhalation on adults in Dhaka City, Bangladesh.

Metal	Pathway	AF	PA	PG	PS	MW	BF	HW	GW	EW	TW	CW	BS
Cr	Ingestion	1.1E-01	1.1E-02	3.1E-03	1.3E-02	2.8E-02	1.7E-02	2.7E-02	2.5E-02	5.1E-03	3.4E-01	1.3E-03	4.4E-03
	dermal	2.4E-04	2.6E-05	7.1E-06	2.9E-05	6.4E-05	3.9E-05	6.3E-05	5.8E-05	1.2E-05	7.8E-04	2.9E-06	1.0E-05
	inhalation	4.6E-04	4.9E-05	1.4E-05	1.1E-04	2.4E-04	1.5E-04	2.4E-04	2.2E-04	4.5E-05	3.0E-03	1.1E-05	3.9E-05
Ni	Ingestion	7.9E-03	1.2E-03	2.7E-03	4.8E-03	3.4E-02	3.4E-03	2.8E-03	2.9E-03	2.9E-03	6.6E-03	9.9E-04	6.6E-04
	dermal	1.8E-05	2.7E-06	6.2E-06	1.1E-05	7.9E-05	7.8E-06	6.4E-06	6.7E-06	6.6E-06	1.5E-05	2.3E-06	1.5E-06
	inhalation	2.6E-04	3.8E-05	8.7E-05	3.1E-04	2.2E-03	2.2E-04	1.8E-04	1.9E-04	1.9E-04	4.3E-04	6.5E-05	4.3E-05
Cu	Ingestion	6.4E-03	1.0E-03	9.4E-04	3.1E-03	1.0E-02	2.2E-03	2.8E-03	3.2E-03	1.5E-03	6.9E-03	7.6E-04	1.0E-03
	dermal	1.5E-05	2.4E-06	2.2E-06	7.1E-06	2.4E-05	5.2E-06	6.5E-06	7.4E-06	3.5E-06	1.6E-05	1.8E-06	2.3E-06
	inhalation	7.5E-06	1.2E-06	1.1E-06	7.2E-06	2.5E-05	5.3E-06	6.6E-06	7.6E-06	3.6E-06	1.6E-05	1.8E-06	2.4E-06
As	Ingestion	1.7E-01	5.8E-02	2.7E-02	6.0E-02	1.8E-01	1.8E-01	1.4E-01	8.6E-02	2.4E-02	3.4E-01	1.5E-02	2.5E-02
	dermal	4.0E-04	1.3E-04	6.3E-05	1.4E-04	4.1E-04	4.1E-04	3.2E-04	2.0E-04	5.6E-05	7.9E-04	3.6E-05	5.7E-05
	inhalation	5.1E-04	1.7E-04	8.0E-05	3.5E-04	1.0E-03	1.0E-03	8.0E-04	5.0E-04	1.4E-04	2.0E-03	9.1E-05	1.5E-04
Cd	Ingestion	5.8E-03	6.3E-03	1.6E-03	9.1E-03	2.5E-02	1.4E-02	1.2E-02	5.9E-03	3.7E-03	2.5E-02	9.9E-04	1.6E-03
	dermal	1.3E-05	1.5E-05	3.7E-06	2.1E-05	5.7E-05	3.1E-05	2.8E-05	1.4E-05	8.5E-06	5.7E-05	2.3E-06	3.6E-06
	inhalation	8.6E-05	9.3E-05	2.3E-06	2.7E-04	7.3E-04	4.0E-04	3.6E-04	1.7E-04	1.1E-04	7.3E-04	2.9E-05	4.6E-05
Pb	Ingestion	4.1E-02	2.1E-02	5.6E-03	1.4E-02	7.9E-02	3.0E-02	4.0E-02	2.9E-02	9.6E-03	2.0E-02	4.4E-03	1.0E-02
	dermal	9.4E-05	4.9E-05	1.3E-05	3.3E-05	1.8E-04	6.9E-05	9.2E-05	6.6E-05	2.2E-05	4.6E-05	1.0E-05	2.3E-05
	inhalation	4.5E-05	2.3E-05	6.3E-06	3.2E-05	1.8E-04	6.6E-05	8.8E-05	6.3E-05	2.1E-05	4.4E-05	9.8E-06	2.2E-05

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Supplementary Information for Chapter 6

Table D.1. Concentration of trace metals (mg/kg) in soil of different geochemical fractions.

Metals	Sampling sites	Geochemical fractions						Total metal
		(Exchangeable)	(Carbonate)	(Fe-Mn oxides)	(Organic)	(Residual)	Total of (F1-F5)	(mg/kg)
Cr	Tf1	0.020	12	119	46	91	268	252±3.8
	Tf2	0.023	30	69	118	112	329	310±6.7
	Tf3	0.024	24	98	50	91	263	203±3.6
	Bf1	0.822	61	122	363	608	1155	1120±41
	Bf2	0.024	42	89	161	247	538	532±4.4
	Bf3	0.028	47	113	99	121	380	377±4.0
	Sf1	0.025	3.9	49	116	114	283	275±8.1
	Sf2	0.426	53	19	24	81	178	166±8.6
	Sf3	0.624	48	46	25	126	246	224±3.8
Ni	Tf1	0.14	33	35	20	48	136	113±8.9
	Tf2	0.24	22	31	43	77	173	140±8.5
	Tf3	0.86	10	15	37	56	117	114±1.1
	Bf1	0.19	17	15	79	180	291	267±1.3
	Bf2	0.32	23	49	63	111	246	225±4.2
	Bf3	0.19	68	32	148	223	471	443±0.5
	Sf1	0.19	25	29	50	69	173	130±2.6
	Sf2	0.08	20	23	31	73	148	131±1.5
	Sf3	0.15	27	32	44	90	194	161±3.4
Cu	Tf1	0.62	38	98	55	48	240	225±14.3
	Tf2	0.43	50	62	97	94	303	295±0.5
	Tf3	0.81	49	39	44	41	173	165±8.3
	Bf1	0.82	58	91	138	195	483	455±3.0
	Bf2	0.94	61	98	235	145	539	510±8.5
	Bf3	0.99	57	76	63	291	487	452±1.1
	Sf1	0.64	18	41	124	81	266	238±10.7

	Sf2	0.84	36	28	62	76	203	174±2.4
	Sf3	0.99	27	62	118	110	318	289±2.2
As	Tf1	0.0030	1.18	13.0	13.5	23.9	51	46±0.9
	Tf2	0.0015	2.79	6.68	22.5	16.5	48	44±1.1
	Tf3	0.0021	4.11	15.9	8.13	21.8	50	41±0.2
	Bf1	0.0132	6.32	19.2	11.4	24.2	61	55±2.9
	Bf2	0.0022	21.3	27.4	42.1	12.1	103	90.4±2.5
	Bf3	0.0085	11.0	22.1	16.1	34.5	84	67±6.7
	Sf1	0.0023	25.3	16.6	11.2	15.2	68	64±2.3
	Sf2	0.0115	20.2	23.8	9.70	34.7	88	81±4.5
	Sf3	0.0016	8.77	17.1	47.1	24.0	97	84±4.3
Cd	Tf1	0.0451	0.81	1.09	0.77	2.90	5.62	4.2±0.2
	Tf2	0.0113	0.70	1.71	1.83	1.76	6.02	4.2±0.4
	Tf3	0.0077	0.50	0.79	2.37	3.97	7.65	6.4±0.9
	Bf1	0.0441	0.47	1.35	2.90	3.30	8.05	6.2±0.2
	Bf2	0.155	1.16	3.00	5.19	1.87	11.37	9.4±0.7
	Bf3	0.0669	2.02	2.54	4.64	4.56	13.82	12.3±0.7
	Sf1	0.0449	0.73	1.69	1.92	2.68	7.06	6.2±0.7
	Sf2	0.0237	0.90	0.63	2.73	3.81	8.09	6.7±1.6
	Sf3	0.0450	0.93	0.89	3.46	3.73	9.06	8.3±0.2
Pb	Tf1	0.0100	6.98	35.2	20.9	36.2	99	89±5.4
	Tf2	0.0111	14.2	29.6	35.4	63.3	142	134±2.1
	Tf3	0.0187	21.3	22.8	19.5	34.8	98	93±1.4
	Bf1	0.341	27.0	28.9	54.3	89.7	200	189±8.8
	Bf2	0.800	44.9	97.8	169	260	572	567±6.7
	Bf3	0.522	31.6	58.8	51.1	109	251	248±0.4
	Sf1	0.0161	14.6	23.6	23.3	75.3	137	132±1.4
	Sf2	0.0133	20.4	27.1	42.0	61.2	151	148±7.4
	Sf3	0.0185	15.9	49.3	34.8	90.6	191	188±1.2

Table D.2. Comparison of metal concentration (mg/kg) [mean (range)] of present study with other study and guideline values.

District (Country)	Description of study site	Cr	Ni	Cu	As	Cd	Pb	References
Dhaka (Bangladesh)	Industrial area	384 (166-1120)	192 (113-443)	311 (165-510)	64 (41-90)	7.12 (4-12)	199 (89-567)	Present study
Noakhali (Bangladesh)	As contaminated site	29 (18-46)	64 (37-93)	22 (13-63)	3.3 (1.5-9.2)	0.07 (0.03-0.2)	13 (8-22)	Rahman et al. (2013)
Dhaka (Bangladesh)	Industrial area	54 (34-68)	58 (36-74)	39 (31-45)	NA	11 (6-16)	50 (44-52)	Ahmad & Goni (2010)
Guandong (China)	Former e-waste site	12.3 (9.66-19)	8.83 (7.04-10.3)	324 (210-450)	NA	0.9 (0.26-1.17)	96 (73-134)	Luo et al. (2011)
Maharashtra (India)	Industrial area	164 (66-279)	171 (69-465)	155 (52-373)	2.8 (NA-11.2)	30 (22-39)	42 (36-49)	Bhagure & Mirgane (2011)
Murcia (Spain)	Industrial area	19.4	17.7	7.4	NA	0.2	18.3	Acosta et al. (2011)
Kayseri (Turkey)	Industrial area	29	44.9	36.9	NA	2.53	74.8	Tokalıoğlu & Kartal (2006)
Background value of Bangladesh soil		NA	22	27	3	0.01-0.2	20	Kashem & Shingh (1999)
Dutch soil quality standard (Target Value)		100	35	36	29	0.8	85	VROM (2000)
Dutch soil quality standard (Intervention Value)		380	210	190	55	12	530	VROM (2000)
Canadian Environmental Quality Guidelines		64	50	63	12	1.4	70	CCME (2003)
Department of Environmental Protection, Australia		50	60	60	20	3	300	DEP (2003)

Table D.3. Metal concentration (mg/kg fw) in vegetables of three riverside agriculture fields near the industrial area, Bangladesh (different letter indicates significant difference at <0.05 level among different vegetables of each river), (n=3).

Location	Local name	Scientific name		Cr	Ni	Cu	As	Cd	Pb
Turag	Brinjal	*Solanum melongena*	Mean±SD	0.58±0.49[a]	2.59±2.65[a]	12.4±7.73[a]	0.057±0.025[a]	0.319±0.087[a]	0.37±0.35[a]
			Range	0.25-1.14	0.74-5.63	7.89-21.33	0.037-0.085	0.22-0.382	0.08-0.75
	Bottle gourd	*Lagenaria siceraria*	Mean±SD	0.47±0.32[a]	2.33±1.79[a]	7.48±3.19[a]	0.036±0.013[a]	0.022±0.022[b]	0.34±0.22[a]
			Range	0.25-0.84	0.79-4.28	4.50-10.84	0.022-0.048	0.007-0.047	0.21-0.60
	Pumpkin	*Cucurbita maxima*	Mean±SD	0.43±0.26[a]	2.25±2.09[a]	7.11±2.37[a]	0.024±0.019[a]	0.006±0.004[b]	0.30±0.21[a]
			Range	0.27-0.73	0.99-4.66	4.86-9.59	0.010-0.046	0.003-0.011	0.16-0.55
	Tomato	*Solanum lycopersicum*	Mean±SD	0.51±0.26[a]	1.28±0.71[a]	9.12±5.08[a]	0.022±0.011[a]	0.087±0.032[b]	0.42±0.41[a]
			Range	0.33-0.80	0.52-1.93	6.00-14.98	0.012-0.033	0.051-0.111	0.15-0.89
Buriganga	Brinjal	*Solanum melongena*	Mean±SD	1.26±0.14[a]	4.00±0.79[a]	21.3±0.22[a]	0.234±0.198[a]	0.466±0.186[a]	1.25±0.86[a]
			Range	1.10-1.38	3.09-4.50	21.1-21.55	0.055-0.447	0.285-0.657	0.51-2.20
	Bottle gourd	*Lagenaria siceraria*	Mean±SD	0.83±0.23[b]	4.29±2.86[a]	13.2±1.10[b]	0.083±0.047[a]	0.049±0.016[b]	2.2±1.37[a]
			Range	0.63-1.08	1.64-7.00	12.1-14.31	0.043-0.135	0.032-0.065	0.97-3.64
	Pumpkin	*Cucurbita maxima*	Mean±SD	0.76±0.12[b]	9.86±0.57[b]	13.5±2.25[b]	0.067±0.028[a]	0.026±0.004[b]	1.21±1.16[a]
			Range	0.69-0.90	9.39-10.50	10.9-14.9	0.051-0.099	0.023-0.030	0.54-2.56
	Tomato	*Solanum lycopersicum*	Mean±SD	0.83±0.06[b]	1.11±0.36[ac]	13.6±0.97[b]	0.066±0.047[a]	0.133±0.027[b]	1.23±0.83[a]
			Range	0.76-0.88	0.71-1.42	12.5-14.2	0.030-0.119	0.084-0.136	0.68-2.18
Shitalakha	Brinjal	*Solanum melongena*	Mean±SD	0.66±0.10[a]	2.70±0.50[a]	13.7±0.91[a]	0.141±0.139[a]	0.485±0.322[a]	0.62±0.12[a]
			Range	0.55-0.76	2.18-3.17	12.7-14.3	0.019-0.292	0.254-0.853	0.48-0.73
	Bottle gourd	*Lagenaria siceraria*	Mean±SD	0.50±0.17[a]	3.67±0.54[a]	9.2±1.65[a]	0.035±0.018[a]	0.108±0.064[ab]	0.59±0.19[a]
			Range	0.31-0.60	3.07-4.11	7.34-10.34	0.016-0.051	0.035-0.152	0.42-0.79
	Pumpkin	*Cucurbita maxima*	Mean±SD	0.67±0.14[a]	2.31±0.35[a]	10.4±1.06[bc]	0.121±0.090[a]	0.028±0.021[b]	0.66±0.29[a]
			Range	0.51-0.75	1.95-2.66	9.41-11.5	0.059-0.225	0.008-0.049	0.32-0.85
	Tomato	*Solanum lycopersicum*	Mean±SD	0.70±0.00[a]	2.38±1.38[a]	11.3±0.79[b]	0.077±0.027[a]	0.133±0.007[ab]	0.89±0.00[a]
			Range	0.70-0.71	0.96-3.70	10.5-12.1	0.052-0.106	0.125-0.138	0.89-0.90
Permissible levels as per (FAO and WHO 2011)				2.3	1.5	10	0.1	0.05	0.1
Chinese standard for metals in vegetables (Li et al. 2012)				0.5	0.3	10	NA	0.05	0.1

The red letters in range cells indicate that the values are exceeding FAO & WHO permissible levels.

Table D.4. Transfer factors for vegetable species calculated using different geochemical faction and total metal concentration in soil.

Metal	Geochemical Fraction	TF of *S. melongena* mean	SD	CV	TF of *L. siceraria* Mean	SD	CV	TF of *C. maxima* mean	SD	CV	TF of *S. lycopersicum* mean	SD	CV
Cr	Exchangeable	30	14	0.47	22	8.6	0.40	23	7.5	0.33	25	7.4	0.29
	Carbonate	0.040	0.051	1.3	0.032	0.047	1.5	0.036	0.059	1.6	0.037	0.054	1.5
	Fe-Mn oxides	0.013	0.008	0.60	0.009	0.004	0.50	0.011	0.011	0.99	0.012	0.010	0.86
	Organic	0.013	0.010	0.80	0.009	0.007	0.80	0.010	0.010	0.92	0.012	0.010	0.88
	Residual	0.006	0.004	0.60	0.004	0.002	0.51	0.005	0.003	0.55	0.005	0.003	0.48
	Total Cr	0.031	0.018	0.57	0.033	0.018	0.54	0.035	0.021	0.60	0.038	0.020	0.53
Ni	Exchangeable	16	9.8	0.63	19	15	0.78	23	20	0.83	10	14	1.3
	Carbonate	0.16	0.17	1.1	0.17	0.15	0.88	0.23	0.22	0.97	0.082	0.068	0.84
	Fe-Mn oxides	0.14	0.12	0.87	0.16	0.14	0.90	0.20	0.22	1.1	0.066	0.051	0.78
	Organic	0.062	0.038	0.62	0.069	0.037	0.53	0.081	0.045	0.56	0.039	0.035	0.90
	Residual	0.035	0.026	0.76	0.037	0.022	0.58	0.044	0.026	0.60	0.020	0.015	0.77
	Total Ni	0.21	0.15	0.70	0.35	0.20	0.57	0.38	0.23	0.59	0.17	0.14	0.79
Cu	Exchangeable	30	4.9	0.16	23	2.4	0.11	23	2.7	0.12	25	2.9	0.12
	Carbonate	0.39	0.18	0.46	1.3	0.13	0.11	0.87	0.15	0.17	0.89	0.15	0.17
	Fe-Mn oxides	0.28	0.15	0.53	0.17	0.076	0.44	0.18	0.086	0.47	0.21	0.11	0.56
	Organic	0.19	0.13	0.70	0.12	0.067	0.57	0.12	0.054	0.46	0.14	0.088	0.64
	Residual	0.17	0.13	0.77	0.11	0.067	0.62	0.11	0.058	0.52	0.13	0.095	0.74
	Total Cu	0.66	0.35	0.54	0.61	0.25	0.40	0.60	0.23	0.38	0.67	0.36	0.53
As	Exchangeable	29	13	0.46	18	20	1.1	27	36	1.3	18	17	0.94
	Carbonate	0.022	0.022	1.0	0.008	0.006	0.73	0.007	0.004	0.50	0.007	0.004	0.55
	Fe-Mn oxides	0.008	0.007	0.89	0.003	0.002	0.54	0.004	0.004	0.95	0.003	0.002	0.60
	Organic	0.012	0.014	1.23	0.003	0.002	0.58	0.005	0.006	1.18	0.004	0.003	0.70
	Residual	0.006	0.005	0.93	0.003	0.003	1.2	0.004	0.005	1.2	0.002	0.001	0.60
	Total As	0.027	0.028	1.0	0.014	0.007	0.49	0.018	0.016	0.89	0.014	0.008	0.58
Cd	Exchangeable	16	14	0.87	2.6	3.1	1.2	0.63	0.47	0.74	4.1	2.8	0.68
	Carbonate	0.52	0.27	0.53	0.070	0.056	0.81	0.025	0.020	0.82	0.14	0.055	0.40
	Fe-Mn oxides	0.39	0.40	1.0	0.062	0.080	1.3	0.019	0.019	1.0	0.092	0.055	0.60
	Organic	0.19	0.13	0.71	0.020	0.016	0.78	0.007	0.004	0.57	0.050	0.033	0.67
	Residual	0.13	0.043	0.33	0.018	0.014	0.78	0.006	0.004	0.71	0.040	0.019	0.48
	Total Cd	0.73	0.35	0.48	0.14	0.12	0.83	0.045	0.030	0.68	0.28	0.11	0.39
Pb	Exchangeable	33	14	0.43	41	22	0.54	33	20	0.62	41	19	0.47
	Carbonate	0.032	0.018	0.55	0.040	0.021	0.53	0.030	0.016	0.52	0.038	0.016	0.42
	Fe-Mn oxides	0.019	0.011	0.56	0.023	0.013	0.55	0.017	0.009	0.55	0.022	0.013	0.57
	Organic	0.018	0.014	0.76	0.020	0.011	0.56	0.015	0.007	0.49	0.021	0.013	0.65
	Residual	0.009	0.007	0.76	0.010	0.005	0.50	0.008	0.004	0.57	0.010	0.007	0.64
	Total Pb	0.047	0.032	0.68	0.081	0.039	0.48	0.057	0.028	0.48	0.075	0.041	0.55

*SD=Standard deviation and CV = Coefficient of variation

Table D.5. Transfer factor (TF) of metals from soil to vegetables calculated using different geochemical fraction values.

Metals	F1 Exchangeable	F2 Carbonate	F3 Fe–Mn oxides	F4 Organic	F5 Residual	Total
Cr	25 (12-49)	0.036 (0.0059-0.19)	0.011 (0.0021-0.039)	0.011 (0.0024-0.031)	0.0052 (0.0014-0.013)	0.034 (0.011-0.073)
Ni	17 (2.2-55)	0.16 (0.010-0.62)	0.14 (0.015-0.70)	0.063 (0.0048-0.15)	0.034 (0.0032-0.10)	0.28 (0.026-0.69)
Cu	15 (8.8-26)	0.30 (0.09-1.3)	0.21 (0.061-0.55)	0.14 (0.046-0.48)	0.13 (0.037-0.52)	0.64 (0.27-1.5)
As	23 (3.3-112)	0.011(0.00063-0.071)	0.0044 (0.009-0.024)	0.0059 (0.00044-0.041)	0.0037 (0.00049-0.019)	0.018 (0.0034-0.095)
Cd	5.9 (0.11-45)	0.19 (0.0044-0.95)	0.14 (0.0018-1.4)	0.066 (0.0017-0.48)	0.049 (0.0016-0.22)	0.3 (0.012-1.49)
Pb	37 (7.7-92)	0.035 (0.011-0.082)	0.02 (0.0022-0.039)	0.019 (0.0037-0.045)	0.0095 (0.0022-0.025)	0.065 (0.010-0.15)

* Values in parentheses show range

APPENDIX E
Supplementary Information for Chapter 7

Table E.1. Trace metal concentrations [mg/kg fw, (mean ± SD)] in most frequently consumed foodstuffs in Dhaka City, Bangladesh

	Foodstuffs	Scientific name	Cr	Ni	Cu	As	Cd	Pb
Cereals	Rice (n=13)	*Oryza sativa*	0.91±0.42	1.4±1.6	6.3±3.1	0.17±0.10	0.057±0.046	0.19±0.32
	Maize (n=8)	*Zea mays*	1.8±0.33	1.3±0.44	2.3±0.39	0.64±0.17	0.075±0.017	0.17±0.08
Pulses	Lentil (n=7)	*Lens culinaris*	1.5±1.3	0.76±0.46	3.3±2.2	0.47±0.29	0.026±0.010	0.47±0.24
	Mung Bean (n=3)	*Vigna radiate*	2.6±1.3	3.0±0.86	4.4±1.6	0.033±0.031	0.007±0.001	0.074±0.02
	Black gram (n=5)	*Vigna mungo*	2.2±1.3	2.8±1.7	4.6±1.4	0.057±0.038	0.014±0.018	0.34±0.25
Vegetables	Brinjal (n=9)	*Solanum melongena*	0.84±0.41	3.1±1.6	16±5.7	0.14±0.14	0.42±0.21	0.75±0.61
	Bottle gourd (n=9)	*Lagenaria siceraria*	0.60±0.28	3.4±1.9	10±3.1	0.052±0.035	0.060±0.051	1.0±1.1
	Pumpkin (n=9)	*Cucurbita maxima*	0.62±0.21	4.8±3.9	10±3.3	0.071±0.064	0.020±0.015	0.72±0.73
	Tomato (n=9)	*Solanum lycopersicum*	0.68±0.19	1.6±1.0	11±3.2	0.055±0.037	0.11±0.029	0.85±0.58
Fruits	Papaya (n=3)	*Carica papaya*	1.5±0.41	0.85±0.48	3.7±1.7	0.22±0.26	0.028±0.044	0.28±0.03
	Banana (n=5)	*Musa paradisiacal*	1.2±1.3	1.0±0.56	4.9±2.5	0.48±0.16	0.049±0.060	0.37±0.22
	Mango (n=3)	*Mangifera indica*	2.1±1.1	0.76±0.76	4.5±3.2	0.41±0.50	0.035±0.04	0.86±0.20
	Jack fruit (n=3)	*Artocarpus heterophyllus*	1.0±0.34	2.3±1.2	8.9±2.6	0.36±0.42	0.042±0.024	0.71±0.31
Fish	Spotted snakehead (n=18)	*Channa punctatus*	2.0±0.90	1.0±0.96	3.0±1.5	0.19±0.093	0.026±0.015	0.63±0.46
	Stinging catfish (n=18)	*Heterponeustes fossilis*	2.1±0.82	1.5±0.75	4.7±1.2	0.27±0.09	0.033±0.013	1.1±0.28
	Banded gourami (n=18)	*Trichogaster fasciata*	2.9±1.1	2.2±0.63	3.5±0.91	0.30±0.09	0.045±0.034	1.3±0.64
Meat	Chicken (n-5)	*Gallus gallus domesticus*	1.4±0.31	0.39±0.43	2.5±1.6	0.032±0.012	0.030±0.032	0.17±0.16
	Beef (n=3)	*Bos primigenius*	1.3±0.24	0.10±0.08	1.2±0.49	0.042±0.015	0.005±0.005	0.17±0.17
	Mutton (n=3)	*Capra aegagrus hircus*	1.2±0.16	1.5±1.6	2.5±1.6	0.042±0.059	0.046±0.063	0.45±0.75
	Chicken egg (n=10)	*Gallus gallus domesticus*	1.4±0.19	1.9±1.8	4.0±2.1	0.087±0.072	0.022±0.024	0.24±0.23
	Cow milk (n=12)	*Bos primigenius*	1.6±0.41	1.5±2.2	2.3±1.2	0.056±0.032	0.029±0.026	0.20±0.23