DETERMINATION AND RISK ANALYSIS OF HEAVY METALS IN DIFFERENT FRUITS COLLECTED FROM DIFFERENT SHOPS OF DHAKA CITY

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CERTIFICATE

This is to certify that the thesis entitled **“DETERMINATION AND RISK ANALYSIS OF HEAVY METALS IN DIFFERENT FRUITS COLLECTED FROM DIFFERENT SHOPS OF DHAKA CITY”** submitted to the Department of Agricultural Chemistry, Faculty of Agriculture, Sher-e-Bangla Agricultural University, Dhaka, in partial fulfillment of the requirements for the degree of **MASTERS OF SCIENCE (M.S.)** in **AGRICULTURAL CHEMISTRY**, embodies the result of a piece of bonafide research work carried out by **SADIA AFRIN**, Registration No. 13-05539 under my supervision and guidance. No part of the thesis has been submitted for any other degree or diploma.

I further certify that any help or source of information, received during the course of this investigation has been duly acknowledged.

June, 2020
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Dedicated to

My

Beloved Parents

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The Author

DETERMINATION AND RISK ANALYSIS OF HEAVY METALS IN DIFFERENT FRUITS COLLECTED FROM DIFFERENT SHOPS OF DHAKA CITY

ABSTRACT

The study was conducted to determine heavy metals in different fruits collected from different shops of Dhaka city at Sher-e-Bangla Agricultural University, Sher-e-Bangla Nagar, Dhaka, during the season 2018-19. Five places *viz.* (1) Shwapno super shop of Mirpur-10, Dhaka, (2) Agora super market, Dhanmondi, Dhaka, (3) Prince Bazar, Mirpur-1, Dhaka, (4) Kawran Bazar fruit market, Kawran Bazar, Dhaka and (5) Meena Bazar, Shyamoli, Dhaka were selected for sample collection. Samples were collected on five fruits namely (i) Grape, (ii) Apple, (iii) Orange, (iv) Banana and (v) Pomegranate. So, twenty five unit samples were considered for the present study which was replicated thrice and remarked as T_1 to T_{25}. The experiment was laid out in Completely Randomized Design (CRD) with three replications. Atomic absorption spectroscopy analysis was used to determine lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni) and cobalt (Co) in sample fruits. It was found that the levels of heavy metals in fruits varied very little from location to location. The mean concentrations of Pb, Cd, Cr, Ni and Co in fruit samples were lower than acceptable limit recommended by FAO/WHO. According to FAO/WHO, the maximum allowable concentration for Pb, Cd, Cr, Ni and Co are 1.50, 0.20, 2.30, 0.80 and 50.00 mg kg^{-1}, respectively. Single factor pollution index (PI) indicates that all fruit samples collected from study area were not yet contaminated. Value of PI<1 indicates that the collected samples are not yet contaminated. In case of sum of pollution index (SPI), samples of Banana found at Kawran Bazar fruit market of Kawran Bazar, Dhaka showed the highest SPI (0.9001) whereas the lowest SPI (0.028) was in Orange found at Agora super market of Dhanmondi, Dhaka. Again, considering, Metal pollution index (MPI), the highest MPI (0.0119) was at Banana found in Meena Bazar of Shyamoli, Dhaka whereas the lowest MPI (0.0025) was in Pomegranate found at Shwapno super shop, Mirpur-10, Dhaka. Proper cultural practice may be an effective measure to reduce heavy metal contamination in fruits. Higher amount of heavy metal intake through fruit consumption can be reduced by regular monitoring of fruit contamination with heavy metals with different methods of heavy metal detections. Presence of heavy metal in fruits regarding Pb, Cd, Cr, Ni and Co is not harmful if it is lower than acceptable limit recommended by FAO/WHO.

According to FAO/WHO it is concluded that there is no health risk for general people in fruit consumption.

LIST OF CONTENTS

Chapter	Title		Page No.
	ACKNOWLEDGEMENTS		i
	ABSTRACT		ii
	LIST OF CONTENTS		iii
	LIST OF TABLES		v
	LIST OF FIGURES		vi
	LIST OF PLATES		vii
	LIST OF APPENDICES		viii
	ABBREVIATIONS AND ACRONYMS		ix
I	**INTRODUCTION**		**1-4**
II	**REVIEW OF LITERATURE**		**5-32**
III	**MATERIALS AND METHODS**		**33-39**
	3.1	Experimental site	33
	3.2	Sampling site and location	33
	3.3	Collection of fruits sample	33
	3.4	Experimental design	35
	3.4.1	Sample chopping	35
	3.4.2	Sun drying	35
	3.4.3	Oven drying	36
	3.4.4	Sample grinding	36
	3.5	Fruits analysis	36
	3.5.1	Sample digestion	36
	3.5.2	Analysis	37
	3.5.3	Standards	37
	3.6	Method validation	37
	3.7	Quality assurance	38
	3.8	Statistical analysis	38
	3.9	Data analysis	38
	3.9.1	Heavy metal limits	38
	3.9.2	Single factor pollution index (PI)	39
	3.9.3	Sum of pollution index (SPI)	39
	3.9.4	Metal pollution index (MPI)	39

LIST OF CONTENTS (Cont'd)

Chapter	Title		Page No.
IV	**RESULTS AND DISCUSSION**		**40-61**
	4.1	Heavy metals in fruit samples collected from Shwapno super shop	40
	4.2	Heavy metals in fruit samples collected from Agora super market	42
	4.3	Heavy metals in fruit samples collected from Agora super market	45
	4.4	Heavy metals in fruit samples collected from Kawran Bazar fruit market	47
	4.5	Heavy metals in fruit samples collected from Meena Bazar of Shyamoli	50
	4.6	Single factor pollution index (PI)	55
	4.7	Sum of pollution index (SPI)	58
	4.8	Metal pollution index (MPI)	60
V	**SUMMARY AND CONCLUSION**		61-64
	REFERENCES		65-90
	APPENDICES		91-93

LIST OF TABLES

Table No.	Title	Page No.
3.1	Sources and places of collection of eggplant samples	34
4.1	Heavy metal concentration in collected fruit samples from Shwapno super shop of Mirpur 10 in Dhaka city	42
4.2	Heavy metal concentration in collected fruit samples from Agora super market of Dhanmondi in Dhaka city	44
4.3	Heavy metal concentration in collected fruit samples from Prince Bazar of Mirpur-1 in Dhaka city	46
4.4	Heavy metal concentration in collected fruit samples from Kawran Bazar fruit market of Kawran Bazar in Dhaka city	50
4.5	Heavy metal concentration in collected fruit samples from Meena Bazar of Shyamoli in Dhaka city	52

LIST OF FIGURES

Figure No.	Title	Page No.
4.1	Single factor pollution index (PI) in fruit samples collected Shwapno super shop, Mirpur-10, Dhaka	55
4.2	Single factor pollution index (PI) in fruit samples collected from Agora super market of Dhanmondi, Dhaka	56
4.3	Single factor pollution index (PI) in fruit samples collected from Prince Bazar of Mirpur-1, Dhaka	57
4.4	Single factor pollution index (PI) in fruit samples collected from from Kawran Bazar fruit market of Kawran Bazar, Dhaka	57
4.5	Single factor pollution index (PI) in fruit samples collected from Meena Bazar of Shyamoli, Dhaka	58
4.6	Sum of pollution index (SPI) in selected fruit samples in the study area	59
4.7	Metal pollution index (MPI) in soil, water, rice grain and rice straw in the study area	60

LIST OF PLATES

Plate No.	Title	Page No.
1.	Photographs showing sample collection and cutting	93

LIST OF APPENDICES

Appendix No.	Title	Page No.
I.	Mean square of heavy metal concentration in collected fruit samples from Shwapno super shop of Mirpur 10 in Dhaka city	91
II.	Mean square of heavy metal concentration in collected fruit samples from Agora super market of Dhanmondi in Dhaka city	91
III.	Mean square of heavy metal concentration in collected fruit samples from Prince Bazar of Mirpur-1 in Dhaka city	91
IV.	Mean square of heavy metal concentration in collected fruit samples from Kawran Bazar fruit market of Kawran Bazar in Dhaka city	92
V.	Mean square of heavy metal concentration in collected fruit samples from Meena Bazar of Shyamoli in Dhaka city	92

ABBREVIATIONS AND ACRONYMS

AEZ	=	Agro-Ecological Zone
BBS	=	Bangladesh Bureau of Statistics
BCSRI	=	Bangladesh Council of Scientific Research Institute
cm	=	Centimeter
CV %	=	Percent Coefficient of Variation
DAS	=	Days After Sowing
DMRT	=	Duncan’s Multiple Range Test
et al.,	=	And others
e.g.	=	exempli gratia (L), for example
etc.	=	Etcetera
FAO	=	Food and Agriculture Organization
g	=	Gram (s)
i.e.	=	id est (L), that is
Kg	=	Kilogram (s)
LSD	=	Least Significant Difference
m^2	=	Meter squares
ml	=	MiliLitre
M.S.	=	Master of Science
No.	=	Number
SAU	=	Sher-e-Bangla Agricultural University
var.	=	Variety
^oC	=	Degree Celceous
%	=	Percentage
NaOH	=	Sodium hydroxide
GM	=	Geometric mean
mg	=	Miligram
P	=	Phosphorus
K	=	Potassium
Ca	=	Calcium
L	=	Litre
µg	=	Microgram
USA	=	United States of America
WHO	=	World Health Organization

CHAPTER I

INTRODUCTION

Plants play a key role in human life, while they are also considered to be predominant medicinal sources for the populations in Bangladesh (Pandey and Madhuri, 2010). Consumption of fruits is essential for a diversified and nutritious diet. Sufficient consumption of fruit and vegetables significantly reduce the incidence of chronic diseases, such as cancer, cardiovascular diseases and other aging-related pathologies (Prakash *et al.*, 2012). Fruits offer protection against free radicals that damage lipids, proteins, and nucleic acids. Polyphenols, carotenoids (pro-vitamin A), vitamins C and E present in fruits have antioxidant and free radical scavenging activities and play a significant role in the prevention of many diseases (Prakash *et al.*, 2012).

Fruits and vegetables are highly nutritious and form as key food commodity in the human consumption. They are highly perishable due to their low shelf life. Recently, (Sharma *et al*., 2008a and Sharma *et al.*, 2008b) have reported that atmospheric deposition can significantly elevate the levels of heavy metals contamination in fruits and vegetables commonly sold in the markets. These food commodities are reported to be contaminated with toxic and health hazardous chemicals. The uptake of heavy metals in vegetables and fruits are influenced by some factors such as climate, atmospheric depositions, concentrations of heavy metals in soil, nature of soil and the degree of maturity of the plants at the time of harvest (Lake *et al.*, 1984 and Scott *et al.*, 1996). Chemicals like calcium carbide/ethephon and oxytocin are reportedly being used in fruit and vegetable farms for artificial ripening of fruits, increasing the size of fruits and vegetables respectively. The major contaminants found in fruit and vegetables are pesticide residues, crop contaminants such as aflatoxins, patulin, ochratoxin etc. and heavy metals. Moreover, direct aspiration of the fruit juices and milk can cause flame fluctuations and accumulation of solid deposits on the burner head (Bellido-Milla *et al.*, 2000).

Heavy metals are non-biodegradable and could persist for a long time in the environment. When vegetables are cultivated in polluted environments, they could readily absorb heavy metals through the leaves or roots, leading to the accumulation of toxic metals in plant tissues (Singh *et al*., 2010). The entry of heavy metals into the food chain not only inhibits the normal physiological functions of the human body, but it also affects the growth, nutrient uptake, nitrogen fixation, and metabolism of plants (Singh *et al*., 2010 and Kumar and Seema, 2016).

Heavy metals are not biodegradable and have the potential for accumulation in the different body organs leading to unwanted side effects (Jarup, 2003 and Sathawara *et al*., 2004). Rapid and unorganized urban and industrial developments have contributed to the elevated level of heavy metals in the urban environment of developing countries (Radwan and Salama, 2006, Maleki and Zarasvand, 2008, Wong *et al*., 2003). Heavy metals are widely dispersed in the environment. Heavy metal contamination of the food items is one of the most important aspects of food quality assurance (Marshall *et al*., 2003). Heavy metals are among the major contaminants of food supply and may considered the most important problem to our environment (Zaidi *et al*., 2005). They enter the food chain and occur in different concentrations in human food (Roychowdhary *et al*., 2003).

The contamination of food with heavy metals is a serious problem. Heavy metals are taken up from the digestive tract and exhibit harmful influence on tissues. The uptake of heavy metals in human digestive tract usually does not exceed 5 to 10 % of their concentration in food. On the other hand, some metals exhibit toxic properties in relatively low doses and moreover their concentration in tissues gradually increases due to accumulation process (Beckett *et al*., 2007). The excessive content of these metals in food is associated with a number of diseases such as cardiovascular, kidney, nervous as well as bone diseases (WHO, 1992, WHO, 1995). Abnormal ingestion causes neurological anomalies, hepatic and renal disturbances (Underwood, 1977). Dietary intake of heavy metals causes carcinogenesis, mutagenesis and teratogenesis (IARC, 1993 and Pitot and Dragan, 1996).

A number of trace elements protect the cell from oxidative cell damage as these minerals are the cofactor of antioxidant enzymes. Zinc, copper and manganese are necessary for superoxide dismutases in both cytosol and mitochondria. Iron is a component of catalase, a hemeprotein, which catalyzes the decomposition of hydrogen peroxide (Machlin and Bendich, 1987). Small amounts of micronutrients are required for good physical condition along with energy food and protein. Sodium, potassium, iron, calcium and many trace elements together with antioxidant vitamins and minerals are vital for the body. Fruits and vegetables have noteworthy amounts of calcium, iron and potassium (Jahan *et al*., 2011). On the other hand, none can guarantee us whether this food item is safe or not as these days rarely any food item is free from food adulteration. Food safety is essential to maintain nutrition, combat food/waterborne diseases, maintain food quality and stop food adulterations, being rampant in Bangladesh.

Heavy metals are a general collective term which applies to the group of metals and metalloids with an atomic density greater than 4 g/cm^3 (Sajib *et al*., 2014). Publicity regarding the concentration of heavy metals in fruits and vegetables will create apprehension and fear in the public as to the presence of heavy metal residues in their daily food. Keeping in mind the potential toxicity and persistent nature of heavy metals, and the frequent consumption of vegetables and fruits, it is necessary to analyze these food items to ensure the levels of these contaminants meet agreed international requirements (Radwan and Salama, 2006).

Considering the above facts it is urgently needed to determine the heavy metal concentrations in fruits. The objective of this work is to estimate the levels of some heavy metals (lead, cadmium, chromium, nickel and cobult) that may be present in fruits available in local or national markets in Dhaka city. Also, the levels of investigated metals were recommended by the international Organization FAO and WHO). Therefore the present study was undertaken with the following objectives:

1. To asses different heavy metals (Pb, Cd, Cr, Ni and Co) from different fruits
2. To interpret the risk of these heavy metals of these fruits (grape, apple, orange, banana and pomegranate)

CHAPTER II

REVIEW OF LITERATURE

Fruits are widely used for culinary purpose. Fruits are very important in human diet because of presence of vitamins and minerals salts. They contain water, calcium, iron, sulphur and potash (Sobukola *et al.*, 2010). They also act as neutralizing agents for acidic substances forming during digestion (Thompson and Kelly 1990). Therefore fruits are very useful for the maintenance of health as a preventive treatment of various diseases (D-mello, 2003). The presence of heavy metals may have a negative influence on the quality of fruits causing changes to their taste and smell. Hence a brief review of available literature with regards to 'determination and risk analysis of heavy metals in different fruits collected from different shops of Dhaka city' is presented in this Chapter.

2.1 Heavy metals and their effects

2.1.1 Lead (Pb)

Lead is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. Lead is a bright silvery metal, slightly bluish in a dry atmosphere. It begins to tarnish on contact with air, thereby forming a complex mixture of compounds, depending on the given conditions (Sharma and Dubey, 2005). The sources of lead exposure include mainly industrial processes, food and smoking, drinking water and domestic sources. The sources of lead were gasoline and house paint, which has been extended to lead bullets, plumbing pipes, pewter pitchers, storage batteries, toys and faucets (Thurmer *et al.*, 2002). In the US, more than 100 to 200,000 tons of lead per year is being released from vehicle exhausts. Some is taken up by plants, fixation to soil and flow into water bodies, hence human exposure of lead in the general population is either due to food or drinking water (Goyer, 1990). Lead is an extremely toxic heavy metal that disturbs various plant physiological processes and unlike other metals, such as zinc, copper and manganese, it does not play any biological functions. A plant with high lead concentration fastens the production of reactive oxygen species (ROS), causing lipid membrane damage that ultimately leads to damage of chlorophyll and photosynthetic processes and suppresses the overall growth of the plant (Najeeb *et al.*, 2014). Some research revealed that lead is capable of inhibiting the growth of tea plant by reducing biomass and debases the tea quality by changing the quality of its components (Yongsheng *et al.*, 2011). Even at low concentrations, lead treatment was found to cause huge instability in ion uptake by plants, which in turn leads to significant metabolic changes in photosynthetic capacity and ultimately in a strong inhibition of plant growth (Mostafa *et al.*, 2012).

Lead metal causes toxicity in living cells by following ionic mechanism and that of oxidative stress. Many researchers have shown that oxidative stress in living cells is caused by the imbalance between the production of free radicals and the generation of antioxidants to detoxify the reactive intermediates or to repair the resulting damage. Antioxidants, as *e.g.* glutathione, present in the cell protect it from free radicals such as H_2O_2. Under the influence of lead, however, the level of the ROS increases and the level of antioxidants decreases. Since glutathione exists both in reduced (GSH) and oxidized (GSSG) state, the reduced form of glutathione gives its reducing equivalents ($H^+ + e^-$) from its thiol groups of cystein to ROS in order to make them stable. In the presence of the enzyme glutathione peroxidase, reduced glutathione readily binds with another molecule of glutathione after donating the electron and forms glutathione disulfide (GSSG). The reduced form (GSH) of glutathione accounts for 90% of the total glutathione content and the oxidized form (GSSG) accounts for 10% under normal conditions. Yet under the condition of oxidative stress, the concentration of GSSG exceeds the concentration of GSH. Another biomarker for oxidative stress is lipid peroxidation, since the free radical collects electron from lipid molecules present inside the cell membrane, which eventually causes lipid peroxidation (Wadhwa *et al.*, 2012; Flora *et al.*, 2012). At very high concentrations, ROS may cause structural damage to cells, proteins, nucleic acid, membranes and lipids, resulting in a stressed situation at cellular level (Mathew *et al.,* 2011).

The ionic mechanism of lead toxicity occurs mainly due to the ability of lead metal ions to replace other bivalent cations like Ca^{2+}, Mg^{2+}, Fe^{2+} and monovalent cations like $Na^{+,}$ which ultimately disturbs the biological metabolism of the cell. The ionic mechanism of lead toxicity causes significant changes in various biological processes such as cell adhesion, intra- and inter-cellular signaling, protein folding, maturation, apoptosis, ionic transportation, enzyme regulation, and release of neurotransmitters. Lead can substitute calcium even in picomolar concentration affecting protein kinase C, which regulates neural excitation and memory storage (Flora *et al.*, 2012).

Lead has a negative influence on both children and adults. For children, Pb reduces the physical growth and mental growth (Simeonov *et al.,* 2010). The intelligent quotient of children is diminished and symptoms of irritability and fatigue could be observed. Pregnant women exposed to Pb have higher rates of infertility, miscarriage and still births (Ediin *et al*., 2000). Chronic exposure to Pb can affect physical growth and can cause anaemia, kidney damage, headache, hearing problems, speaking problems, fatigue or irritable mood (Simeonov *et al*., 2010). The toxicity of Pb is multiple biochemical effects. It has the ability to inactivate enzymes, compete with calcium for incorporation into bones and interfere with nerve transmission and brain development (Ediin *et al*., 2000).

The WHO maximum allowed contaminant level in the water is 0.01 mg/l (Monudu and Anyakora, 2010). The main sources of Pb in the environment include, dust from leaded paints from older houses, leaded gasoline and tap water from soldered pipes (Ediin *et al*., 2000). Indoor chemicals and indoor smoking is also a source (Simeonov *et al*., 2010). Mebrahtu and Zerabruk (2011) in their study of concentration of heavy metals in drinking water from urban areas of the Tigray Region, Northern Ethiopia using atomic absorption spectroscopy method of analysis detected levels of Pb of 1.347 mg/l at Indasilase and a minimum of below detection limit in drinking water samples from Alamata, Korem, Hagereselam, Zelambessa, Firewoini, Axum, Adwa and Enticho. More than 70.15 % of the water samples analyzed contained lead concentration within the WHO (2003) maximum allowable limit of lead in drinking water. In a similar research carried out by Kaplan *et al*. (2011) at Tunceli in Turkey, Pb was only detected in drinking water from one station, out of the sampled. The highest value of Pb detected was 0.31µg/l and this was below the maximum permissible limit for lead in water.

Similar results were obtained by Wogu and Okaka (2011) in a study on heavy metals in Warri river in Nigeria. They recorded a variation of Pb levels in water ranging from 0.0 to 0.001 mg/l which were below the maximum WHO (2003) permissible limits of lead in drinking water of 0.01 mg/l. A similar study by Raji *et al.* (2010) recorded the following Pb levels in water in the following stations; station T_1, 0.720 mg/l, station T_2, 0.390 mg/l, station T_3, 0.310 mg/l, station WB(R), 0.340 mg/l and station WB (T), 0.350 mg/l. In the soils, the maximum allowable limits of lead in UK and USA are 100 mg/kg and 200 mg/kg (Mamtaz and Chowdhury, 2006).

A study carried out by Mico *et al.* (2006) on heavy metal content of agricultural soils in a Mediterranean Semiarid Segura River Valley in Spain recorded 19.6 mg/kg of Pb in the soil and a lead level range of 8.9 mg/kg-34.5 mg/kg. The soil samples were analyzed by flame atomic absorption spectroscopy. A study by Ijeoma *et al.* (2011), on heavy metal content in high traffic area soils of Pakistan, recorded a minimum lead concentration of 10.06 mg/kg and a maximum Pb concentration of 29.71 mg/kg. A study by Atiemo *et al*. (2010) recorded levels of Pb in road soils ranging from 33.640 mg/kg to 117.45 mg/kg. Similarly Jaradat and Momani (1999) recorded levels of Pb in roadside soils at different distances from the road ranging from 3.70 mg/kg to

272.20 mg/kg.

Human activities such as mining, manufacturing and fossil fuel burning has resulted in the accumulation of lead and its compounds in the environment, including air, water and soil. Lead is used for the production of batteries, cosmetics, metal products such as ammunitions, solder and pipes, *etc.* (Martin and Griswold, 2009). Lead is highly toxic and hence its use in various products, such as paints, gasoline, *etc.*, has been considerably reduced nowadays. The main sources of lead exposure are lead based paints, gasoline, cosmetics, toys, household dust, contaminated soil, industrial emissions (Gerhardsson *et al.*, 2002). Lead poisoning was considered to be a classic disease and the signs that were seen in children and adults were mainly pertaining to the central nervous system and the gastrointestinal tract (Markowitz, 2000). Lead poisoning can also occur from drinking water. The pipes that carry the water may be made of lead and its compounds which can contaminate the water (Brochin *et al.*, 2008). According to the Environmental Protection Agency (EPA), lead is considered a carcinogen. Lead has major effects on different parts of the body. Lead distribution in the body initially depends on the blood flow into various tissues and almost 95% of lead is deposited in the form of insoluble phosphate in skeletal bones (Papanikolaou 2005). Toxicity of lead, also called lead poisoning, can be either acute or chronic. Acute exposure can cause loss of appetite, headache, hypertension, abdominal pain, renal dysfunction, fatigue, sleeplessness, arthritis, hallucinations and vertigo. Acute exposure mainly occurs in the place of work and in some manufacturing industries which make use of lead. Chronic exposure of lead can result in mental retardation, birth defects, psychosis, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness, brain damage, kidney damage and may even cause death (Martin and Griswold, 2009). Although lead poisoning is preventable it still remains a dangerous disease which can affect most of the organs. The plasma membrane moves into the interstitial spaces of the brain when the blood brain barrier is exposed to elevated levels of lead concentration, resulting in a condition called edema (Teo *et al.* 1997). It disrupts the intracellular second messenger systems and alters the functioning of the central nervous system, whose protection is highly important. Environmental and domestic sources of lead ions are the main cause of the disease but with proper precautionary measures it is possible to reduce the risk associated with lead toxicity (Brochin *et al.*, 2008).

2.1.2 Cadmium (Cd)

Cadmium is the seventh most toxic heavy metal as per ATSDR (Agency for Toxic Substances and Disease Registry) ranking. It is a by-product of zinc production which humans or animals may get exposed to at work or in the environment. Once this metal gets absorbed by humans, it will accumulate inside the body throughout life. This metal was first used in World War I as a substitute for tin and in paint industries as a pigment. In today's scenario, it is also being used in rechargeable batteries, for special alloys production and also present in tobacco smoke. About three-fourths of cadmium is used in alkaline batteries as an electrode component, the remaining part is used in coatings, pigments and platings and as a plastic stabilizer. Humans may get exposed to this metal primarily by inhalation and ingestion and can suffer from acute and chronic intoxications. Cadmium distributed in the environment will remain in soils and sediments for several decades. Plants gradually take up these metals which get accumulated in them and concentrate along the food chain, reaching ultimately the human body. In the US, more than 500,000 workers get exposed to toxic cadmium each year as per The Agency for Toxic Substances and Disease Registry (Bernard, 2008; Mutlu *et al.*, 2012). Researchers have shown that in China the total area polluted by cadmium is more than 11,000 hectares and its annual amount of industrial waste of cadmium discharged into the environment is assessed to be more than 680 tons. In Japan and China, environmental cadmium exposure is comparatively higher than in any other country (Han *et al.*, 2009). Cadmium is predominantly found in fruits and vegetables due to its high rate of soil-to-plant transfer (Satarug *et al.*, 2011). Cadmium is a highly toxic nonessential heavy metal that is well recognized for its adverse influence on the enzymatic systems of cells, oxidative stress and for inducing nutritional deficiency in plants (Irfan *et al.*, 2013).

The mechanism of cadmium toxicity is not understood clearly but its effects on cells are known (Patrick, 2003). Cadmium concentration increases 3,000 fold when it binds to cystein-rich protein such as metallothionein. In the liver, the cystein-metallothionein complex causes hepatotoxicity and then it circulates to the kidney and gets accumulated in the renal tissue causing nephrotoxicity. Cadmium has the capability to bind with cystein, glutamate, histidine and aspartate ligands and can lead to the deficiency of iron (Castagnetto *et al.*, 2002). Cadmium and zinc have the same oxidation states and hence cadmium can replace zinc present in metallothionein, thereby inhibiting it from acting as a free radical scavenger within the cell.

Cd is a heavy metal characterized by high mobility in biological systems. It is emitted to the atmosphere in combustion processes, mainly in the form of oxides and Cd uptake by plants is partly limited by presence of calcium, phosphorus and chelating compounds in the soil (Wieczorek *et al*., 2004). The exposure of Cd and especially chronic exposure can cause renal dysfunction, calcium metabolism disorders and also increased incidence of some forms of cancer (Selinus and Alloway, 2005). In plants, Cd induces oxidative stress in plant cells and inactivates some enzymes (Wieczorek *et al*., 2004).

Cd taken up by plants from the soil accumulates first of all in the roots, and then transported in smaller quantities to stems and seeds (Wieczorek *et al*., 2004). Among the sources of Cd in the environment include; mining and smelting of metal ores, fossil fuel combustion and also phosphate fertilizers and Cd is also used in the production of nickel-Cd rechargeable batteries that become deposited in sewage sludge, thus raising environmental levels of Cd (Challa and Kumar, 2009). Farming practices such as tobacco growing also increases the level of Cd in the environment as tobacco is known to accumulate in its tissues (Selinus and Alloway, 2005). The sources of Cd in the urban areas are much less well defined than those of Pb, but metal plating and tire rubber were considered the likely sources of Cd within Kirisia Commercial area which houses Maralal town (Jaradat and Momani, 1999).

Cd is also found in lubricating oils as part of many additives and car tyres as a result of the vulcanization process. In the absence of any major industry in the sampling sites, the levels of Cd could be due to lubricating oils and/or old tires, that are frequently used, and the rough surfaces of the roads which increase the wearing of tires (Jaradat and Momani, 1999). At higher concentrations, it is known to have a toxic potential. The other sources of Cd are industrial activities; the metal is widely used in electroplating, pigments, plastics, stabilizers and battery industries (Mehbrahtu and Zerabruk, 2011). Cd is highly toxic and responsible for several cases of poisoning through food. Small quantities of Cd cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures and kidney damage (Mehbrahtu and Zerabruk, 2011). The maximum contaminant level of Cd allowed in water by WHO is 0.003 mg/l (Monudu and Anyakora, 2010). The recommended concentration in the soils is 3 mg/l (Adeleken and Abegunde, 2011). A study by Wogu and Okaka (2011) on Warri river water in the Delta region of Nigeria, recorded a Cd mean level of 0.0072 mg/l in the water and a range of 0.0 to 0.04 mg/l of Cd the water. The maximum value of Cd that was detected in the water was above the maximum permissible level of Cd in drinking water.

A similar study carried out by Singh and Chandel (2006) on heavy metals of industrial effluents at Jaipur, Rejasthan in India, Cd was undetected in all the samples that were tested. A study by Kisamo (2003) on the environment hazards associated with heavy metals in Lake Victoria Basin reported levels of Cd in soils ranging from 0.16 mg/l to 0.55 mg/l. The range recorded in the above study was below the WHO maximum permissible limit of Cd set at 3 mg/l. A similar study by Mwegoha and Kihampa (2010) on heavy metal contamination in agricultural soils in Dar es Salaam city recorded values below detection limit in all the water samples analyzed. A study by Delbari and Kulkarni (2011) recorded Cd values in agricultural soils ranging from 0.000 to 0.004 mg/l with a mean value of 0.002 mg/kg in summer season and 0,001 to 0.004 mg/kg with the mean value of 0.002 mg/kg in winter season. Similarly, Jaradat and Momani (1999) recorded Cd levels in roadside soils ranging from 0.21 mg/kg to 0.75 mg/kg.

Cadmium is a metal of the 20th century. It is a byproduct of zinc production. Soils and rocks, including coal and mineral fertilizers, contain some amount of cadmium. Cadmium has many applications, *e.g.* in batteries, pigments, plastics and metal coatings and is widely used in electroplating (Martin and Griswold, 2009). Cadmium and its compounds are classified as Group 1 carcinogens for humans by the International Agency for Research on Cancer (Henson and Chedrese, 2004). Cadmium is released into the environment through natural activities such as volcanic eruptions, weathering, river transport and some human activities such as mining, smelting, tobacco smoking, incineration of municipal waste, and manufacture of fertilizers. Although cadmium emissions have been noticeably reduced in most industrialized countries, it is a remaining source of fear for workers and people living in the polluted areas. Cadmium can cause both acute and chronic intoxications (Chakraborty *et al.*, 2013). Cadmium is highly toxic to the kidney and it accumulates in the proximal tubular cells in higher concentrations. Cadmium can cause bone mineralization either through bone damage or by renal dysfunction. Studies on humans and animals have revealed that osteoporosis (skeletal damage) is a critical effect of cadmium exposure along with disturbances in calcium metabolism, formation of renal stones and hypercalciuria. Inhaling higher levels of cadmium can cause severe damage to the lungs. If cadmium is ingested in higher amounts, it can lead to stomach irritation and result in vomiting and diarrhea. On very long exposure time at lower concentrations, it can become deposited in the kidney and finally lead to kidney disease, fragile bones and lung damage (Bernard, 2008). Cadmium and its compounds are highly water soluble compared to other metals. Their bioavailability is very high and hence it tends to bioaccumulate. Long-term exposure to cadmium can result in morphopathological changes in the kidneys. Smokers are more susceptible for cadmium intoxication than non-smokers. Tobacco is the main source of cadmium uptake in smokers as tobacco plants, like other plants, can accumulate cadmium from the soil. Non-smokers are exposed to cadmium via food and some other pathways. Yet cadmium uptake through other pathways is much lower (Mudgal *et al.*, 2010). Cadmium interacts with essential nutrients through which it causes its toxicity effects. Experimental analysis in animals has shown that 50% of cadmium gets absorbed in the lungs and less in the gastrointestinal tract. Premature birth and reduced birth weights are the issues that arise if cadmium exposure is high during human pregnancy (Henson and Chedrese, 2004).

2.1.3 Chromium (Cr)

Chromium (Cr) with atomic number 24, molecular weight 51.1 and density 7.19 g/cm3 is a silver color hard metal. Chromium is the 7th most abundant element (Nriagu, 1988), and 21st most abundant metal (Sinha *et al.*, 2005; Economou-Eliopoulos *et al.*, 2013) of the Earth's crust. Chromium is one of the 18 core hazardous air pollutants (HAPs), 33 urban air toxicants, 188 HAPs (US EPA), and has been ranked 7^{th} among the top 20 hazardous substances by the Agency for Toxic Substances and Disease Registry (Oh *et al.*, 2007). This metal is ranked 5^{th} among the heavy metals in the Comprehensive Environmental Response, Compensation, and Liability Act (Ma *et al.*, 2007). Chromium is also categorized as no.1 carcinogen according to the International Agency for Research on Cancer (IARC, 1987) and the National Toxicology

Program. Therefore, this metal requires detailed understanding and in-depth monitoring in the environment, especially soil-plant system.

Environmental contamination of Cr has gained substantial consideration worldwide because of its high levels in the water and soil originating from numerous natural and anthropogenic activities (Quantin *et al*., 2008; Ashraf *et al*., 2017). Chromium eventually accumulates in crops from contaminated soils, and imparts severe health risks in humans via food chain contamination (Broadway *et al*., 2010; Ahmed *et al*., 2016). Soil-plant transfer of Cr is controlled by numerous factors related to plant physiology (plant type, rate and type of root secretions, root surface area and transpiration) and soil properties (texture, pH, cation exchange capacity) (Banks *et al*., 2006; Santos and Rodriguez, 2012). In the majority of plant species, Cr is poorly translocated towards aerial parts and is mainly retained in the root tissues (Jaison and Muthukumar, 2016). However, Cr-hyperaccumulators such as atlantic cord grass (*Spartina argentinensis*), jelutong (*Dyera costulata*) and spleen amaranth (*Amaranthus dubius*) can uptake and translocate high Cr levels in shoot tissues (D-Oliveira *et al*., 2016).

Chromium does not have any known biological role in physiological and biochemical metabolism of plants (Reale *et al*., 2016). Of what is generally conceived, excessive Cr level in plant tissues can provoke numerous physiological, morphological, and biochemical toxic effects (Uddin *et al*., 2015; Kamran *et al*., 2016). Metal toxicity is generally attributed to a very complex system of metal interactions with genetic processes, signal and metabolic pathways and cellular macromolecules (Santos and Rodriguez, 2012; Eleftheriou *et al*., 2015; Kumari *et al*., 2016). Chromium toxicity is well-reported to reduce plant growth, cause ultrastructural modifications of the cell membrane and chloroplast, persuade chlorosis in leaves, damage root cells, reduce pigment content, disturb water relations and mineral nutrition, and alter enzymatic activities (Ali *et al*., 2015; Farooq *et al*., 2016; Reale *et al*., 2016).

High levels of Cr in plants also induce changes in the physiology and morphology of plants due to enhanced generation of reactive oxygen species (ROS) (Islam *et al.*, 2014; Eleftheriou *et al.*, 2015; Gill *et al.*, 2015). ROS, when generated at high levels, may provoke cell death because of oxidative processes such as mutilation of DNA and RNA, inhibition of enzyme, lipid peroxidation, and protein oxidation (Shahid *et al.*, 2015). Numerous studies report that Cr toxicity suppresses the functioning and regulation of various proteins (Dotaniya *et al.*, 2014) and causes chromosomal aberrations in plant tissues (Kranner and Colville, 2011). In order to cope with high levels of ROS produced under biotic and abiotic stresses, plants have developed numerous complex adaptive strategies, including chelation by organic molecules followed by sequestration within vacuoles (Shahid *et al.*, 2014; Prado *et al.*, 2016). Plants also possess a secondary mechanism of producing antioxidant enzymes to scavenge the enhanced levels of Cr-mediated ROS (Yadav *et al.*, 2010; Pourrut *et al.*, 2011). Therefore, it is critically important to understand the biogeochemistry of Cr in soil-plant environment, and the impacts that high levels of Cr will endure on the ecosystem.

Chromium is a heavy metal is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$. Major sources of Cr contamination include releases from electroplating processes and the disposal of Cr containing wastes (Smith *et al.*, 1995). Chromium(VI) is the form of Cr commonly found at contaminated sites. Chromium can also occur in the +III oxidation state, depending on pH and redox conditions. Major Cr(VI) species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) which precipitate readily in the presence of metal cations (especially Ba^{2+}, Pb^{2+}, and Ag^{+}). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Chromium(III) is the dominant form of Cr at low pH (<4). Cr^{3+} forms solution complexes with NH_3, OH^-, Cl^-, F^-, CN^-, SO_4^{2-} and soluble organic ligands. Chromium (VI) is the more toxic form of chromium and is also more mobile. Chromium(III) mobility is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5 due to the formation of $Cr(OH)_3(s)$ (Chrostowski *et al.*, 1991). Chromium mobility depends on sorption characteristics of the soil, including clay content, iron oxide content, and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater. The leach ability of Cr(VI) increases as soil pH increases. Most of Cr released into natural waters is particle associated, however, and is ultimately deposited into the sediment (Smith *et al.*, 1995). Chromium is associated with allergic dermatitis in humans (Scragg, 2006).

Naturally Cr occurs as chromite ($FeCr_2O_4$) in serpentine or ultramafic rocks or as a constituent of vauquelinite ($CuPb_2CrO_4^-$ PO_4OH), tarapacaite (K_2CrO_4), bentorite ($Ca_6(CrAl)_2(SO_4)_3$) and crocoite ($PbCrO_4$) (Avudainayagam *et al.*, 2003; Babula *et al.*, 2008). Chromium may persist in original minerals, co-precipitated with manganese (Mn), aluminum (Al), and/or iron (Fe) oxides and hydroxides, which are generally adsorbed on soil particles, and complexed with soil organic compounds (Hsu *et al.*, 2015). The concentration of Cr in the parent rocks vary greatly: sedimentary and igneous rocks contain low Cr levels (5-120 ppm), while ultramafic (1600-3400 ppm) and mafic (170-200 ppm) rocks have higher Cr concentration and the average concentration of Cr in limestone ranges from 5-16 mg kg^{-1} (Kabata-Pendias, 2010).

Natural level of Cr in the Earth's crust varies in the range of 0.1-0.3 mg kg^{-1}. However, different studies reported different natural, average and background levels of Cr in soil. Majority of the soils contain Cr levels in the range of 15-100 µg g^{-1} and it increases with clay contents. Chromium concentration in the fresh water ranges from 0.1 to 117 µg L^{-1}, while sea water contains Cr concentration of 0.2-50 mg L^{-1} (Nriagu, 1988).

The acceptable level in soil for the protection of environmental and human health has been estimated at 64 mg kg^{-1} (CCME, 2015). The threshold limits for Cr(III) concentration in sea water, fresh water, and irrigation water are 50, 8, and 5 mg L^{-1}, while for Cr(VI) these values are 1, 1, and 8 mg L^{-1}, respectively (Zayed and Terry, 2003). Most of the monitoring agencies of different countries have recommended 50 mg L^{-1} Cr (VI) as the maximum allowable limit in the drinking water (Lilli *et al*., 2015). The maximum contaminant level of 100 mg L^{-1} in drinking water has been set by USEPA and ATSDR.

Among heavy metals, Cr is reported to be least mobile element in the plant roots (Shukla *et al*., 2007). Concentration of Cr in roots is sometimes 100-times higher than the shoots (Shanker *et al*., 2005). In *Pisum sativum* plants, compartmentation of Cr in the different plant parts was in the following order: roots > stem > leaves > seed (Tiwari *et al*., 2009). Caldelas *et al*. (2012) found the highest Cr concentration in the cell walls of roots and in the cytoplasm and intercellular spaces of the rhizome of Iris pseudacorus. Liu *et al*. (2009) reported that cell wall fraction contained major portion of Cr (83.2%) in roots, while vacuole and cytoplasm fraction accumulated 57.5% of leaf Cr.

Cr (III) uptake in plants is a passive mechanism and does not require any energy by the plants (Shanker *et al*., 2005). On the other hand, Cr (VI) uptake by plants is an active process (generally via phosphate or sulfate transporter) because of structural resemblance of Cr (VI) with phosphate and sulfate (D-Oliveira *et al*., 2014; D-Oliveira *et al*., 2016). Presence of sulfate in growth medium inhibits Cr (VI) uptake by plants (D-Oliveira *et al*., 2014). The interaction of Cr (VI) with sulfate is reinforced by the fact that Cr (VI) exposure to plants induces almost the same effects as sulfur starvation, which is attributed to competition for uptake as well as in subsequent assimilation pathways (Pereira *et al*., 2008).

2.1.4 Nickel (Ni)

Nickel is a transition element with atomic number 28 and atomic weight 58.69. In low pH regions, the metal exists in the form of the nickelous ion, Ni(II). In neutral to slightly alkaline solutions, it precipitates as nickelous hydroxide, $Ni(OH)_2$, which is a stable compound. This precipitate readily dissolves in acid solutions forming Ni(III) and in very alkaline conditions; it forms nickelite ion, $HNiO_2$, that is soluble in water. In very oxidizing and alkaline conditions, nickel exists in form of the stable nickelo-nickelic oxide, Ni_3O_4, that is soluble in acid solutions. Other nickel oxides such as nickelic oxide, Ni_2O_3, and nickel peroxide, NiO_2, are unstable in alkaline solutions and decompose by giving off oxygen (Pourbaix, 1974).

Nickel is 22nd most abundant element on earth crust (twice as Cu) and an important trace metal (Hussain *et al.*, 2013). It comprises approximately 0.008% of earth crust (Hedfi *et al.*, 2007). Approximately 10% of Ni in earth crust is being locked up in molten Fe-Ni ore (Ahmad *et al.*, 2011). Ni has several oxidation states ranging from −1 to 4 however, Ni (II) is the most common state found in biological systems (Denkhaus and Salnikow, 2002). It readily forms Ni-containing alloys found in increasing variety of uses in modern world. Numerous Ni compounds such as Ni acetate, Ni carbonate, Ni hydroxide and Ni oxide are widely used in industries for manufacturing a variety of products.

Ni is released into the air by power plants and trash incinerators and settles to the ground after undergoing precipitation reactions. It usually takes a long time for nickel to be removed from air. Nickel can also end up in surface water when it is a part of wastewater streams. The larger part of all Ni compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result (Anoduadi *et al.*, 2009).

Nickel is an essential microelement for normal plant growth and development and part of several biological functions (Brown, 2007). It is an integral part of several enzymes such as glyoxalase-I and urease required for nitrogen metabolism in higher plants (Mustafiz *et al*., 2014). Ni being a vital element contributes significant role in nitrogen assimilation as well as helps plants against numerous biotic and abiotic stresses (Sreekanth *et al*., 2013). Therefore, Ni deficiency in plants may lead to affect negatively and symptoms such as retarded plant growth, senescence, reduced N metabolism and reduced Fe uptake can be seen in Ni-deficient plants (Brown, 2007; Chen-Huang and Liu, 2009). Although Ni is an essential element, it may cause toxicity at higher concentrations and could lead to several deleterious alterations in plants (Rahman *et al*., 2005).

Excessive Ni results in Ni toxicity and symptoms like leaf chlorosis may appear with addition to growth inhibition, reduced photosynthesis and respiration, and mineral nutrition disorders, sugar transport and water relations (Seregin and Kozhevnikova, 2006). Ni toxicity also plays a prominent role in inhibition of plant root growth, but it is difficult to show a comprehensive mechanism because Ni toxicity affects several metal ions and metabolic pathways (Baccouch *et al*., 2001).

Environment Agency (2009e) documented that nickel from anthropogenic sources is more readily taken up by plants than that from natural occurring sources, and that plant species also differ in their tolerance and ability to take up nickel from soils. Nickel toxicity levels vary widely between 25 to 50 ppm (Mishra and Kar, 1974). However, Gregson and Hope (1994) reported that the phytotoxic concentrations of nickel occurred at leaf contents of 10 to 100 ppm depending on the plant species, while, Kabata- Pendias and Pendias (2001) reported phytotoxic range of 40 to 246 ppm DW plant tissue, depending on the plant species and cultivars.

Dermal absorption of nickel through human skin is quite very limited, and its uptake from soil is rather fewer. Moody *et al*. (2009) studied an in vitro dermal absorption of radioactive nickel chloride through human breast skin for a period of 24 h with and without a spiked reference soil; the obtained results revealed a mean dermal absorption of 1% with soil and 23% without soil presence. Further studies showed that most nickel applied as a soluble salt is bound within the skin and does not reach systematic circulation (Hostynek *et al.*, 2001; Turkhall *et al.*, 2008), hence, nickel allergy in the form of contact dermatitis is a very common and well- known reaction in animals and humans, and is related to nickel induced hypersensitivity and skin disorders (USEPA, 1986).

Food intake is the major route of nickel exposure for the general population, while inhalation from air, drinking water, oral and dermal routes could serve as secondary sources of nickel exposure. Nickel naturally occur in foodstuffs at a general range of 0.1 to 0.5 ppm, but few number of foods usually obtain nickel during the manufacturing process or through food processing methods that may arise from leaching from stainless steel, the milling of flour or through the catalytic hydrogenation of fats and oils (Clarkson,1988; Solomons *et al.*,1982).

Heavy metal pollution is one of the most dramatic threats to the environment and living organisms (Wo-Niak and Basiak, 2003). Among all the environmental pollutants, nickel (Ni) is one of the ubiquitous trace metals emitted in the environment through both natural and anthropogenic activities (Salt *et al.*, 2000). Release of Ni into the environment is of great concern including its deposition in agricultural soils (Salt *et al.*, 2000; Jamil *et al.*, 2014).

In recent years, Ni pollution has been reported from across the world, including Asia, North America and Europe (Papadopoulos *et al.*, 2007). According to an estimation, Ni concentrations can reach up to 26 g/kg and 0.2 mg/L in polluted soils and surface water respectively, which is 20–30 times higher than unpolluted areas (Cempel and Nikel, 2006). Therefore, soil and water contamination with Ni has become a serious problem worldwide seeking wise solutions to be addressed (Thakali *et al.*, 2006).

Seregin and Kozhevnikova (2006) reported that Ni stress has detrimental effects on ultrastructure of leaves and thickness of mesophyll cells, size of vascular bundles, vessel diameter and width of leaf epidermal cells of wheat. Molas (1998) showed that excessive Ni decreased volume of intercellular spaces, palisade and mesophyll sponge in Brassica oleracea plants. In addition to the disruption of general metabolic processes, Ni toxicity is also known to reduce the plasticity of cell walls (Shi and Cai, 2009).

Elevated levels of Ni in the soil altered various physiological process in plants and toxicity symptoms including chlorosis and necrosis were observed in numerous plant species especially in rice (*Oryza sativa* L.) (Pandey and Sharma, 2002). Membrane functionality disruption and ion balance in cytoplasm are the major consequences of Ni toxicity in plants (Saad *et al*., 2016).

Flyvholm *et al*., (1984) reported increase of nickel intake of up to 900 µg/ person/ day or more on large consumption of rich food sources of nickel that include dark chocolate and soya products, dried beans and peas, as well as oat meal. The toxic effects of nickel result from its ability to replace other metal ions in enzymes, proteins or bind to cellular compounds (Cempel and Nikel, 2006), and among animals, micro-organisms and plants, nickel is reported by Nielsen (1980) to interact with at least 13 essential elements namely calcium, chromium, cobalt, copper, iodine, iron, magnesium, manganese, molybdenum, phosphorus, potassium, sodium and zinc.

Several studies have been conducted addressing the toxic effects of heavy metals on biological membranes and integrity (Shahzad *et al*., 2017, 2018). These toxic effects are closely related to the overproduction of reactive oxygen species (ROS) that has damaging effects on cell membranes, proteins, lipids and DNA through lipid peroxidation (Anjum *et al*., 2016a; b), leading to the development of impairments and genetic instability in plant species (Bal and Kasprzak, 2002).

Therefore, prolong exposure to oxides and sulphides of nickel is associated with possible risk to lung and nasal tumours, while systematic effects whose initial symptoms are mild nausea, headache, dyspnoea, and chest pain could be ascribed to nickel carbonyl; these symptoms may disappear or consequently results in severe pulmonary insufficiency. Also, arising from exposure to nickel containing mists and dusts are asthma, pneumoconiosis and irritation of nasal membranes (Kabata- Pendias and Pendias, 1992; El- Hinnawi and Hashmi, 1988).

Nickel is often mobile, can translocate to seeds, and leaves which enhances its potential to enter food chain. Accumulation of higher concentrations of Ni in plants has severe implications in human and animals (Cullaj *et al*., 2004). Hyperaccumulator plants can store high concentration of hazardous metals which may affect the human and animal health through entering in food chain. The consequence of phytoremediation is accumulating sizeable volume of contaminated and hazardous biomass; this menacing biomass should be properly disposed-off to avoid health and environmental risks. This hazardous biomass is composed of organic matter, ash, cellulose, lignin and hemicellulose and have high moisture and volatile component, having caloric value (Mohanty and Patra, 2011) depending upon the plant species. Entry of this biomass to food chain can cause serious health disorders in human and animals (Cempel and Nikel, 2006). Therefore, plant species selected for phytoremediation should be non-edible, disease resistant and can only be used for renewable energy source.

2.1.5 Cobalt (Co)

In the periodic table of elements, cobalt is classified as a transition metal (Koch *et al*., 2007). It has both chalcophile, siderophile and lithophile properties. Its chalcophility manifests itself mainly in the fact that it can occur in the form of sulfides in the lowest parts of the Earth’s mantle (Lock *et al*., 2006), while cobalt siderophility is related to its low affinity to oxygen and sulfur, which makes this metal soluble in liquid nitrogen and able to occur in the Earth's core. Cobalt also occurs in the silicate layer of the Earth's crust, which indicates litophile properties. It is assumed that the natural cobalt content in the Earth's crust does not exceed 12 mg·kg^{-1} (Sheppard *et al.*, 2007).

The contamination of soil with cobalt have the effect on other trace elements in soil, e.g. they may be increased the content of lead, chromium, nickel and zinc in soil (Kosiorek and Wyszkowski, 2019c). Cobalt is released during the weathering process in the oxidation state of +2 and is then strongly bound by the mineral and organic-mineral complex in a readily- and slowly-exchangeable form (Swarnalatha *et al.*, 2013). Due to ion exchange and chemical processes, cobalt is adsorbed by clay minerals, which results in the formation of complex compounds on their surface (Li *et al.*, 2009).

A naturally high soil cobalt level is closely linked to manganese and iron presence as well as organic soils. This is due to the high susceptibility of the oxides of these metals to binding and adsorbing the cations of divalent and trivalent cobalt, as well as easy sorption by organic matter (DávilaRangel and Solache-Ríos, 2006). It is assumed that loamy and alluvial soils have naturally high cobalt contents of up to 12 mg kg^{-1}, and podsolic and silty soils have the lowest, with a mean cobalt content of only 5.5 mg kg^{-1}. Compared to the average cobalt content in the world's soils, this value is not much higher than the lowest cobalt content in sandy and silty soils, where it is 8 mg kg^{-1}. However, soils formed from bedrock with a high cobalt content can contain up to 500 mg kg^{-1} of this element (Tappero *et al.*, 2007).

Cobalt mobility in soils is low (Edwards *et al.*, 2012). It is assumed that over 95% of cobalt after prior introduction into the soil does not move and it remains in the soil down to a depth of around 5 cm. Increasing the acidity and anaerobic soil conditions causes the cobalt mobility to increase (Narendrula *et al.*, 2012). The main cause of this tendency is the inhibition of valence bonds with Fe and Mn. However, since divalent cobalt and manganese ions do not have strong complex formation abilities, the outer hydration shell is not destroyed during their binding (Lalah *et al.*, 2009).

Application of different substances (e.g. manure, zeolite, calcium oxide) to soil reduced the content of cobalt and other trace elements in soil (Kosiorek and Wyszkowski, 2019c). These materials (especially manure) have a positive effect on the available forms of phosphorus, potassium and magnesium, total nitrogen and other properties of soil (Kosiorek and Wyszkowski, 2019b).

Cobalt is the trace element which have a strong effect on growth and development of plants. The negative effect of soil contamination with cobalt on plants depends on many other factors e.g. soil reaction, content of organic matter, clay and other macronutrients and micronutrients in soil. The result of cobalt presence in the soil is its accumulation in plants, also including in their fruits (Soylak *et al.*, 2012).

Cobalt availability to plants largely depends on the soil conditions (Agbenin, 2009). This was confirmed in a study by Edwards *et al.* (2012) where the application of drainage in pasture soil accelerated the weathering of minerals and increased cobalt absorption by grasses. The accumulation rate for aquatic plants mainly depends on such factors as temperature, salinity and water oxygen concentration (Chatterjee and Dube, 2005).

Cobalt presence in plants also allows the proper course of metabolic and growth processes to be maintained (Collins and Kinsela, 2011; Soylak *et al.*, 2012). According to Trejo-Tapia *et al.* (2001) cobalt content in plants has a positive effect on the production of betalains and secondary metabolites and cobalt is also responsible for leaf pigmentation in leguminous plants (Rancelis *et al.*, 2012). It also plays a significant role during ethylene synthesis inhibition in sunflower, which was confirmed by Benlloch-González *et al.* (2010).

Cobalt toxicity is closely related with the acidity of the soil. In alkaline soil the toxic effect of cobalt contamination on plant development is smaller than in acid soil. For higher plants, no effect of cobalt on their growth and development has been shown (Rognerud *et al*., 2013). However, to meet the nutritional requirements, cobalt content in their tissues should not be lower than 0.08 mg/kg. Among papilionaceous plants, clovers have the greatest accumulative abilities and among cereals, wheats have the highest. In vegetables, cabbage and lettuce are characterized by the highest cobalt contents (Nirmal-Kumar *et al*., 2007).

An excessive soil cobalt content, apart from reducing plant growth and development, can affect the absorption of other elements by plants. In a study by Wyszkowski *et al*. (2009) soil contamination with cobalt caused a decrease content of potassium, phosphorus, sodium, magnesium and especially calcium in the aboveground parts of oats. In another experiment by Wyszkowski and Wyszkowska (2007) low cobalt doses (10-20 mg Co·kg-1 soil) had a small effect on macronutrient content in spring barley. Its very high doses (320 mg $Co \cdot kg^{-1}$ soil) caused increased contents of all macronutrients, especially calcium, sodium and nitrogen, in the aboveground parts of this plant. In experiment by Kosiorek and Wyszkowski (2019a) the contamination of soil with cobalt increased the concentration of nitrogen, phosphorus, sodium, calcium in all organs of oat (grain, straw and roots). Chatterjee and Chatterjee (2003) point out a high increase in phosphorus content and Gopal *et al*. (2003) a decrease in phosphorus and protein and non-protein nitrogen in plants under the influence of cobalt.

Increased cobalt absorption by aquatic animals is also affected by the amount of mobile forms of this element accumulated in the bottom sediments of lakes, rivers and seas (Mohiuddin *et al*., 2012; Jayasiri *et al*., 2014). A particular risk to these animals is posed by sediments near highly populated places or places impacted by different industry branches and on the edge of water bodies (Swarnalatha *et al*., 2013; Chanpiwat and Sthiannopkao, 2014). A change in physicochemical water conditions is an additional factor causing increased cobalt release to waters (Ochieng *et al*., 2008; Zamani-Hargalani *et al*., 2014).

Cobalt in the human body, as in animals, performs an important role in the formation of vitamin B12 (Dobrowolski and Otto, 2012). According to ATSDR (2004) 0.1 µmol of cobalt in the form of vitamin B12 supplies a necessary amount of cobalt to the human body. The highest cobalt intake which does not cause negative effects is 1800 µmol. Vitamin B_{12} deficiency is supplemented, apart from its supply in plant and animal products to the human body, also by the application of drugs (Ulusoy *et al*., 2012). Its deficiency in the human body leads to the appearance of anemia, resulting from a low amount of produced vitamin B12. Another manifestation of a cobalt deficiency in the human body is disturbed functioning of the alimentary, nervous and osseous systems (Jonnalagadda *et al*., 2008; Soylak *et al*., 2012). The disease symptoms resulting from exceeding the permissible dose include, among others, allergic reactions, lung and heart diseases (Basu *et al*., 2010; Devi *et al*., 2014). Intensification of the above symptoms is most often encountered in industrial plants, where exposure to the harmful effect of this element is much higher than in other places with a human presence (Benderli-Cihan *et al*., 2011; Pietrodangelo *et al*., 2014).

Basu *et al*. (2010) and Ryuko *et al*. (2012) report that the most frequent symptoms of cobalt excess are skin inflammations and asthma. Frequent use of tools which contain cobalt admixtures, as well as the presence in industrial plants, significantly affects the induction of allergic reactions, mainly on the skin of the hands. The occupations particularly exposed to such risks are carpenters and metal workers (Thyssen *et al*., 2011).

The harmful effect of cobalt can also be the result of absorbing its too high dose with food and drinking water (Obiri, 2007; Upadhyaya *et al*., 2014). This is particularly important for pregnant women who, depending on the type of consumed food, can accumulate substantial amounts of cobalt in their bodies, which also affects the developing fetus. This was confirmed by Chan-Hon-Tong *et al*. (2013) who found that a group of tested pregnant women eating mainly fish had a higher blood cobalt content than the women consuming sweets, fruit, milk products and soups. A study by Foster *et al*. (2012) did not find, however, differences in the blood cobalt content of pregnant women depending on consumed food. Due to genotoxic properties, it is important that the cobalt limit is not exceeded (Chan-Hon-Tong *et al*., 2013).

2.2 Heavy metal status in different fruits

Verma *et al*. (2016) focuses on the toxicity level of heavy metals among the common man in urban areas and the level of heavy metal contamination in fruits and fruit juices. Heavy metals normally occur in nature and are essential to life but can become toxic through accumulation in organisms. Heavy metals also cause adverse effect in human metabolic system, skin diseases, heart problems, etc. Arsenic, cadmium, chromium, copper, nickel, lead and mercury are the most common heavy metals. Sources of heavy metals include mining, industrial production, smelters, petrochemical plants, pesticide production, chemical industry, untreated sewage sludge and diffuse sources such as metal piping, traffic and combustion by-products etc. Fruits and vegetables are highly nutritious form as key food commodity in the human consumption. These food commodities are reported to be contaminated with toxic and health hazardous chemicals. Trace levels of heavy metals such as Fe, Pb, Cu and Cd were determined in 5 different varieties of fruits sample such as apple, banana, pomegranate, grapes and orange purchased from local market of Lucknow. The study shows that, the urban consumers are at greater risk of purchasing fresh fruits with high levels of heavy metals beyond the legally permissible limits. Fe (450.21 ìg/g) and Pb (224.4 ìg/g) concentration was found higher than other metal.

Ezigbo and Obiageli (2015) found the concentrations of some heavy metals such as lead (Pb), Cadmium (Cd), Cobalt (Co) and Selenium (Se) present in common fruit spices available at local markets in Nigeria were determined using Atomir Absorption Sprectrophotometry (AAS). The study showed differences in metal concentrations according to the locations. The concentration of lead (Pb) ranged from trace to 12-30 mg kg^{-1} on dry weigh basis where as that of cadmium (Cd) was ranged from 1.20 mg kg^{-1} to 3.00 mg kg^{-1}.The concentration level of cobalt was from zero to 0.60 mg kg^{-1}. While variable levels of selenium were detected from zero to 12.05 mg kg^{-1}. Some of these concentrations are above the standard limit approved by WHO and FAO. No risk from daily intake of the most of fruit spices under study for hazardous Pb, Cd, Co and Se if the human take about 20g of spices per day. But there are dangerous from thyme and ginger for lead.

Elbagermi *et al*. (2014) showed that the average concentrations detected ranged from 0.02 to 1.824, 0.75 to 6.21, 0.042 to 11.4, 0.141 to 1.168, 0.19 to 5.143, and 0.01 to 0.362 mg/kg for Pb, Cu, Zn, Co, Ni, and Cd, respectively. The content of lead (Pb), copper (Cu), zinc (Zn), cobalt (Co), nickel (Ni), and cadmium (Cd) in some selected fruits and vegetables from the Misurata City Market, Libya, were measured using atomic absorption spectrophotometry. The highest mean levels of Pb, Cu, Zn, Co, Ni and Cd were detected in mango, melon, spinach, banana, mango, and mango fruits, respectively. The levels of these metals found in our study are compared with those reported for similar fruits and vegetables from some other parts of the world. The daily human intakes of Pb, Cu, Zn, Co, Ni, and Cd ascribed to a diet of fruits and vegetables in this region have also been estimated.

Sajib *et al*. (2014) were determined heavy metals namely arsenic, cadmium, lead, mercury and chromium content of ten tropical fruits to assess their concentration as these days rarely any food item is spared from the malicious practice of food adulteration. Fruits and vegetables are specially valued in human diet as these contain micronutrients, fiber, potassium, vitamin C, which work as antioxidants within the body as well as bio-functional components.

Minerals and heavy metals content of ten tropical fruits namely Sapodilla (*Manilkara zapota*), Stone-apple (*Aegle marmelos*), Indian- gooseberry (*Phyllanthus emblica*), Guava (*Psidium guajava*), Bilimbi (*Averrhoa bilimbi*), Elephant-apple (*Dillenia indica*), Tamarind fruit (*Tamarindus indica*), Mango (*Mangifera indica*), Litchi (*Litchi chinensis*), Strawberry (*Fragaria ananassa*) were determined according to standard methods to address their concentration. Results of this study suggest that the selected tropical fruits are rich source of minerals. Tamarind fruit is an ample source of iron, sodium, potassium, calcium and magnesium. Highest amount of manganese found in Mango, 06.16 ± 1.19 mg. Highest amounts of copper, zinc and sodium found in Guava, 19.30 ± 2.12 mg, 2.07 ± 0.15 mg and 62.78 ± 1.24 mg, respectively. Highest amount of iron, potassium, calcium and magnesium found in Tamarind fruit, 2.80 ± 1.43 mg, 621.00 ± 3.26 mg, 75.00 ± 2.41 mg and 90.00 ± 1.80 mg, respectively. The consequences of this study indicate that these tropical fruits could be potentially used in alleviating micronutrients deficiency especially for the rural populace as a potent source of minerals and the daily intake of heavy metals through fresh fruits may not constitute a health hazard for consumers because the concentrations were below than the recommended daily intake of these metals but consumers should be aware of taking fresh fruit as these amounts can be harmful if the fruits are taken in large quantities.

All heavy-metals levels were below permissible limits except ‘lead’ (Pb) on vegetables which was 1.8-3.5 times higher. The highest hazard index (42%) found in waste water irrigated cabbage (Lente *et al*., 2013). Leafy vegetables like Amaranthus have more scavenging capacity for Cd and Pb, while Spinacia Oleracea has more scavenging capacity for chromium (Kumar *et al*., 2013). Vegetable production of Solanum melongena was negatively affected by the presence of heavy metals in Kolkatta, India. The concentration of Cd, Cr, Pb, Ni and Hg were found to be higher than the WHO, FAO permissible limit in Solanum melongena (Nandi *et al*., 2012).

Four sites in Ranchi city, Bihar were analyzed for metal contamination. The concentration ranges (ppm) were 13.733-20.667 for Pb in peas, 0.3333-4.333 for Ni, 1.167- 2.933 for Ni and 0.100-0.800 for Cd in cucumber, 0.267- 0.867 for Cd in coriander (Ghosh *et al.*, 2011). According to market basket survey of some Egyptian fruits and vegetables, the average concentrations (mg kg^{-1}) for Pb, Cd, Cu and Zn were found to be 0.01-0.87, 0.01-0.15, 0.83-18.3 and 1.36-20.9, respectively (Radwan and Salama, 2006).

Sobukola *et al*. (2010) conducted a study on heavy metals levels in sixteen different fruits and leafy vegetables from selected markets from Lagos, Nigeria were determined heavy metals using atomic absorption spectrometry. The results showed that in banana, orange and watermelon the levels of Lead, Cadmium, Copper, Zinc, Cobalt, Nickel , cadmium and copper were observed to be the lowest for the samples while the levels of nickel and lead were the highest. Pb in fruits were observed in, banana, apple and watermelon (0.30 mg/kg); orange (0.15mg/kg) and banana (0.02 mg/kg). Cadmium is all sample analyzed level varying between 0.003 and 0.09 mg/kg; watermelon (0.02 and 0.0004 mg/kg); orange (0.04 and 0.0009 mg/kg) and .banana (0.02 and 0.001 mg/kg). Copper is concentrations of Cu in all the tested samples varied between 0.002 and 0.07 mg/kg; with orange, watermelon 0.002 - 0.006 and banana or zinc level watermelon, orange and banana, respectively. However, 0.011 and 0.014 mg/kg.

Mahdavian and Somashekar (2009) conducted a study with samples of fruits (grape, pomegranate, orange, banana, lemon, pear, apple, sapota, mango and guava), and vegetables (brinjal, cucumber, tomato, capsicum, cauliflower, bean, radish, carrot, bottle gourd, chilly, root beet, onions, potatoes, lady's finger, cabbage, garlic) were procured fromthe Bangalore citymarkets during the period from May through November 2007 with the objective of determining their heavy metals composition *viz.*, lead, zinc, cadmium, copper, cobalt, chromium, iron, manganese and nickel. The samples were digested and analysed for heavy metals using flame atomic absorption spectrophotometer. The results showed that urban consumers are at greater risk of getting exposed to heavy metals through fresh vegetables and fruits because of higher levels of heavy metals beyond the legally permissible limits as defined by FAO/WHO. The results indicated the order of abundance of heavy metals in fresh vegetables samples as Fe > Mn > Pb > Co > Cu > Zn > Ni > Cr > Cd, and in fruits as Fe > Cr > Mn > Pb > Ni > Co > Zn > Cu > Cd.

CHAPTER III

MATERIALS AND METHODS

This chapter includes the details of the materials and methods of this research work. The experimental materials, site, experimental design, collection of fruits samples etc. are described under their headings below. This study was undertaken during the season 2018-19 for the determination and risk analysis of heavy metals in different fruits collected from different shops of Dhaka city.

3.1 Experimental site

Primarily the raw sample were washed and cut in the Agricultural Chemistry Department Laboratory of Sher-e-Bangla Agricultural University. Then initial samples were dried in oven in the Laboratory. The samples were grinded and digested in the Laboratory of Soil Science, BARI (Bangladesh Agricultural Research Institute), Gazipur, Bangladesh.

3.2 Sampling site and location

Samples were collected from four super shops located in Dhaka city. They were:

Sl. No.	Name of super shop	Outlets Location
1	Shwapno	Mirpur 10
2	Agora	Dhanmondi
3	Prince Bazar	Mirpur 1
4	Kawran Bazar fruit market	Kawran Bazar
5	Meena Bazar	Shyamoli

3.3 Collection of fruits sample

Samples were collected randomly from 05 (five) outlets of Dhaka city. They were arranged in shelves in wet condition under light. Twenty five samples were collected from respected outlets and each sample was replicated thrice, thus the total 25 × 3 = 75 samples from all outlets in different amount as below:

Three samples of each fruits from each market were collected and the amount of fruits collected for each sample is given below:

Kinds of fruits	**Amount**
Grapes	1000 g
Apple	1000 g
Orange	1000 g
Banana	1000 g
Pomegranate	1000 g

The amount of fruits samples was more or less same. The fruits samples were put into the individual polythene bag with definite marking and tagging and kept in fridge at temperature of around 0°C as the sample collection was not possible at a time. After collecting all the samples from all the outlets, rotten parts and other extraneous materials were removed. Then they were washed in cool water and then kept in air tight polythene bag by tagging in fridge again until preparing for drying. Sources and places of collection of fruit samples are presented in Table 1.

Table 3.1**:** Sources and places of collection of fruit samples

Area of collection	**Sample ID**	**Source**
Shwapno super shop	T_1 (Grape) T_2 (Apple) T_3 (Orange T_4 (Banana) T_5 (Pomegranate)	Mirpur 10, Mirpur, Dhaka
Agora super market	T_6 (Grape) T_7 (Apple) T_8 (Orange T_9 (Banana) T_{10} (Pomegranate)	Dhanmondi, Dhaka

Prince Bazar	T_{11} (Grape) T_{12} (Apple) T_{13} (Orange T_{14} (Banana) T_{15} (Pomegranate)	Mirpur 1, Mirpur, Dhaka
Kawran Bazar fruit market	T_{16} (Grape) T_{17} (Apple) T_{18} (Orange T_{19} (Banana) T_{20} (Pomegranate)	Kawran Bazarfruit market, Kawran Bazar, Dhaka
Meena Bazar	T_{21} (Grape) T_{22} (Apple) T_{23} (Orange T_{24} (Banana) T_{25} (Pomegranate)	Shyamoli, Dhaka

3.4 Experimental design

Subsamples were taken at random. Collected Samples were prepared for experiment in this way:

3.4.1 Sample chopping

Samples stored in freeze firstly kept in normal temperature for sometimes. Then they were kept in chopping board and chopped by a sharp knife. The chopped sample pieces were near about 0.5 inch. This operation was done in the Laboratory of Agricultural Chemistry Department of Sher-e-Bangla Agricultural University, Dhaka, Bangladesh.

3.4.2 Sun drying

The chopped sample pieces were kept under sun light for 7 days. It was done for partial drying. When the samples lost their wet condition they were packed by aluminum foil.

3.4.3 Oven drying

The sun dried samples were kept in racks of the Drying Oven. Then the Oven was set at 45°C for 24 hours and 30°C for next 24 hours. As all of the samples could not be to dry at a time so the sun dried samples were kept in air tight poly bags. Over drying operation of sundried samples were done in the Laboratory of Agricultural Chemistry Department of Sher-e-Bangla Agricultural University, Dhaka, Bangladesh.

3.4.4 Sample grinding

All the samples were powdered manually in a grinder individually. The grinded samples were kept in air tight poly bags.

3.5 Fruits analysis

3.5.1 Sample digestion

The fruits sample weighing 0.5 g was transferred into a dry clean digestion vessel. 10 mL Nitric Acid (HNO_3) was added to the vessel and allowed it for 30 minutes to heat at 95-105°C. Then the sample allowed standing it for overnight with covering the vessel to vapor recovery device. The following day, the digestion vessel was placed on a heating block and was heated at a temperature slowly raised to 115-120°C until the digestion became clear. After cooling, 2 mL of Hydrogen Per oxide (H_2O_2) was added and kept for few minutes. Again the vessel was heated at 120-125°C. Heating was stopped when the liquid sample was clear after which the volume was reduced to 5 mL. The digest was cooled, diluted to 50 mL with de-ionized water and filtered through Whatman No. 42 filter paper into plastic bottle (Hoque, 2003). Sample digestion procedure was completed in the Laboratory of Agricultural Chemistry Department of Sher-e-Bangla Agricultural University, Dhaka, Bangladesh.

3.5.2 Analysis

Collected digested samples were brought to the Laboratory of Soil Science, BARI (Bangladesh Agricultural Research Institute), Gazipur, Bangladesh. Concentration of heavy metals in the acidic solution was estimated using Atomic absorption spectrophotometer, (Chemito Technologies Pvt. Ltd., India, Model No - AA - 203, Slit width 0.5 nm). Estimations were carried out using the hollow cathode lamps depending upon the element to be tested. The results were expressed as $\mu g\ g^{-1}$ **(**on a dry weight basis).

3.5.3 Standards

Standard solutions of the heavy metals namely lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni) and cobalt (Co) was provided by Merck (Darmstadt, Germany). The standards were prepared from the individual 1000 mg/L standards (Merck) supplied in 0.1 N HNO_3.

3.6 Method validation

The digestion method and atomic absorption spectroscopy analysis (AAS; model- AA-7000) were validated by recovery method. One gram of randomly selected sample was spiked with three different concentrations of heavy metals one at a time (1.0, 1.5, 2.0 ppm) each run in with the AAS 44 machine. This was followed by the digestion of the spiked samples and determination of metal concentration using AAS. Blank or unspiked samples were digested through the same process and analyzed by same AAS. The amount that was recovered after digestion of the spiked samples was used to calculate % recovery (Al-weher, 2008). A mean recovery of the matrix was evaluated at 95% confidence level (Borosova *et al*. 2002).

3.7 Quality assurance

Appropriate quality assurance procedures and precautions were taken to ensure the reliability of the results. Samples were carefully handled to avoid cross contamination. Glassware was properly cleaned, and reagents used were of analytical grades. De-ionized water was used throughout the study. Reagent blank determinations were used to apply corrections to the instrument readings.

3.8 Statistical analysis

The experiment was laid out in Completely Randomized Design (CRD). Mean concentrations of heavy metals in fruits were analyzed using ANOVA technique by MSTAT-C software. One way analysis of variance (ANOVA) was used to determine significant difference ($p<0.05$) between groups. The Duncan's Multiple Range Test (DMRT) with Least Significant Difference value was determined with appropriate levels of significance and the means were tabulated (Gomez and Gomez, 1984).

3.9 Data analysis

Content of heavy metals in fruits samples was estimated. Apart from content, following parameters were assessed to estimate risk associated with uptake of metals:

3.9.1 Heavy metal limits

Standard limits of heavy metal is presented in Table 3.1 with reference of FAO/WHO, 2011.

Table 3.1 Heavy metal limits (allowable limit) in different sources showing references

Source	Heavy metal limit for human consumption (mg/kg)					References
	Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)	
Fruits	1.5	0.20	2.30	0.80	50.00	FAO/WHO, 2011

3.9.2 Single factor pollution index (PI)

The pollution index (PI) is the ratio of metal concentration in a biotic or abiotic medium to that of the regulatory Standard of International bodies such as World Health Organization (WHO), United States Environmental Protection Agency (USEPA) Food and Agriculture Organization (FAO) (Jamali *et al.*, 2007).

Mathematically, PI is expressed as:

$PI = C_{fruit} / C_{FAO/WHO\text{-}standard}$

Where PI is the individual pollution index **of** study metal,

C_{fruit} is the concentration of the metal in plant.

$C_{FAO/WHO\text{-}standard}$ is the value of the regulatory limit of the heavy metal by FAO/WHO

3.9.3 Sum of pollution index (SPI)

Sum of Pollution index (SPI) described by Qingjie *et al*. (2008) was used for the present application.

SPI = PIPb+ PICd+ PICr+ PINi+ PICo

Where, PI = Single factor pollution index of heavy metals

3.9.4 Metal pollution index (MPI)

To examine the overall heavy metal concentrations in fruits, the metal pollution index (MPI) was computed by Usero *et al.*, 1997. This index was obtained by calculating the geometrical mean of concentrations of all the metals.

$$MPI\ (mg\ kg^{-1}) = (C_1 \times C_2 \times C_3 \times \ldots\ldots\ldots \times C_n)^{1/n}$$

Where, C_n = Concentration of metal n in the sample

CHAPTER IV

RESULTS AND DISCUSSION

The findings of the study are presented here under the following headings.

4.1. Heavy metals in fruit samples collected from Shwapno super shop

Table 4.1 shows different fruit samples collected from Shwapno super shop of Mirpur-10, Dhaka containing different detected heavy metal. Total fifteen samples of different fruits (three samples of each of five fruits *viz*. Grape, Apple, Orange, Banana and Pomegranate) were analyzed to find out the heavy metal contamination (Pb, Cd, Cr, Ni and Co).

Non-significant variation was found in terms of different heavy metal concentration of Pb, Cd, Cr, Ni and Co in different fruit samples collected from Shwapno super shop, Mirpur-10, Dhaka (Table 4.1 and Appendix I).

Consideration of Pb (Lead) concentration, it is ranged from 0.04 to 0.10 mg kg^{-1} among the fruit samples. Results indicated that the highest Pb concentration (0.10 mg kg^{-1}) was found in T_4 (Banana) whereas samples from T_1 (Grape) showed lowest Pb concentration (0.04 mg kg^{-1}). Fruit sample T_5 (Pomegranate) also showed Pb concentration compared to other fruit samples collected from Shwapno super shop of Mirpur-10, Dhaka. Maximum allowable concentration of Pb in sampled fruits under consideration of health risk given by FAO/WHO is 1.50 mg kg^{-1} (Table 4.1) which is higher than Pb content in collected fruit samples. So, according to FAO/WHO (2011), Pb content in collected fruit samples from Shwapno super shop of Mirpur-10, Dhaka might not be risk for health in terms of over Pb content.

Consideration of Cd (Cadmium) concentration, it is ranged from 0.001 to 0.003 mg kg^{-1} among the fruit samples. Results indicated that the highest Cd concentration (0.003 mg kg^{-1}) was found in T_1 (Grape) whereas samples from T_2 (Apple), T_3 (Orange) and T_4 (Banana) showed lowest Cd concentration

(0.001 mg kg^{-1}). Maximum allowable concentration of Cd in sampled fruits under consideration of health risk given by FAO/WHO is 0.20 mg kg^{-1} (Table 4.1) which is higher than Cd content in collected fruit samples. So, according to FAO/WHO (2011), Cd content in collected fruit samples from Shwapno super shop of Mirpur-10, Dhaka may not be risk for health in terms of over Cd content.

Consideration of Cr (Chromium) concentration, it is ranged from 0.001 to 0.002 mg kg^{-1} among the fruit samples. Results indicated that the highest Cr concentration (0.002 mg kg^{-1}) was found in T_1 (Grape) and T_2 (Apple) whereas samples from T_3 (Orange), T_4 (Banana) and T_5 (Pomegranate) showed lowest Cr concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Cr in sampled fruits under consideration of health risk given by FAO/WHO is 2.30 mg kg^{-1} (Table 4.1) which is higher than Cr content in collected fruit samples. So, according to FAO/WHO (2011), Cr content in collected fruit samples from Shwapno super shop of Mirpur-10, Dhaka might not be risk for health in terms of over Cr content.

In terms of Ni (Nickel) concentration, it is ranged from 0.001 to 0.003 mg kg^{-1} among the fruit samples. Results indicated that the highest Ni concentration (0.003 mg kg^{-1}) was found in T_4 (Banana) whereas samples from T_1 (Grape), T_2 (Apple) and T_5 (Pomegranate) showed lowest Ni concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Ni in sampled fruits under consideration of health risk given by FAO/WHO is 0.80 mg kg^{-1} (Table 4.1) which is higher than Ni content in collected fruit samples. So, according to FAO/WHO (2011), Ni content in collected fruit samples from Shwapno super shop of Mirpur-10, Dhaka might not be risk for health in terms of over Ni content.

Table 4.1. Heavy metal concentration in collected fruit samples from Shwapno super shop of Mirpur 10 in Dhaka city

Treatment	Heavy metal concentration in fruit samples (mg/kg) collected from Shwapno super market, Mirpur 10, Dhaka				
	Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)
T_1 (Grape)	0.04	0.003	0.002	0.001	0.002
T_2 (Apple)	0.05	0.001	0.002	0.001	0.002
T_3 (Orange)	0.06	0.001	0.001	0.002	0.001
T_4 (Banana)	0.10	0.001	0.001	0.003	0.001
T_5 (Pomegranate)	0.09	0.001	0.001	0.001	0.001
$LSD_{0.05}$	NS	NS	NS	NS	NS
CV(%)	3.64	2.88	2.17	2.52	1.36
MAC (FAO/WHO, 2011)	1.50	0.20	2.30	0.80	50.00

*MAC = Maximum allowable concentration

Consideration of Co (Cobalt) concentration, it is ranged from 0.001 to 0.002 mg kg^{-1} among the fruit samples. Results indicated that the highest Co concentration (0.002 mg kg^{-1}) was found in T_1 (Grape) and T_2 (Apple) whereas samples from T_3 (Orange), T_4 (Banana) and T_5 (Pomegranate) showed lowest Co concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Co in sampled fruits under consideration of health risk given by FAO/WHO is 50.00 mg kg^{-1} (Table 4.1) which is higher than Co content in collected fruit samples. So, according to FAO/WHO (2011), Co content in collected fruit samples from Shwapno super shop of Mirpur-10, Dhaka might not be risk for health in terms of over Co content.

4.2 Heavy metals in fruit samples collected from Agora super market

Table 4.2 shows different fruit samples collected from Agora super market of Dhanmondi, Dhaka containing different detected heavy metal. Total fifteen samples of different fruits (three samples of each of five fruits *viz*. Grape, Apple, Orange, Banana and Pomegranate) were analyzed to find out the heavy metal contamination (Pb, Cd, Cr, Ni and Co).

Significant variation was found in terms of Pb concentration in different fruit samples but non-significant variation was observed in terms of Cd, Cr, Ni and Co concentration in different fruit samples collected from Agora super market of Dhanmondi, Dhaka (Table 4.2 and Appendix II).

Regarding Pb (Lead) concentration, it is ranged from 0.02 to 0.21 mg kg^{-1} among the fruit samples. Results indicated that the highest Pb concentration (0.21 mg kg^{-1}) was found in T_9 (Banana) which was significantly different from other samples. Again, the sample from T_8 (Orange) showed lowest Pb concentration (0.02 mg kg^{-1}) which was significantly same with T_6 (Grape) and T_7 (Apple). Maximum allowable concentration of Pb in sampled fruits under consideration of health risk given by FAO/WHO is 1.50 mg kg^{-1} (Table 4.2) which is higher than Pb content in collected fruit samples. So, according to FAO/WHO (2011), Pb content in collected fruit samples from Agora super market of Dhanmondi, Dhaka might not be risk for health in terms of over Pb content.

Consideration of Cd (Cadmium) concentration, it is ranged from 0.001 to 0.004 mg kg^{-1} among the fruit samples. Results indicated that the highest Cd concentration (0.004 mg kg^{-1}) was found in T_7 (Apple) and T_9 (Banana) whereas samples from T_{10} (Pomegranate) showed lowest Cd concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Cd in sampled fruits under consideration of health risk given by FAO/WHO is 0.20 mg kg^{-1} (Table 3.1) which is higher than Cd content in collected fruit samples. So, according to FAO/WHO (2011), Cd content in collected fruit samples from Agora super market of Dhanmondi, Dhaka may not be risk for health in terms of over Cd content.

In case of Cr (Chromium) concentration, it is ranged from 0.002 to 0.006 mg kg^{-1} among the fruit samples. Results indicated that the highest Cr concentration (0.006 mg kg^{-1}) was found in T_9 (Banana) whereas samples from T_{10} (Pomegranate) showed lowest Cr concentration (0.002 mg kg^{-1}). Maximum allowable concentration of Cr in sampled fruits under consideration of health risk given by FAO/WHO is 2.30 mg kg^{-1} (Table 3.1) which is higher than Cr content in collected fruit samples. So, according to FAO/WHO (2011), Cr content in collected fruit samples from Agora super market of Dhanmondi, Dhaka might not be risk for health in terms of over Cr content.

In terms of Ni (Nickel) concentration, it is ranged from 0.001 to 0.004 mg kg^{-1} among the fruit samples. Results indicated that the highest Ni concentration (0.004 mg kg^{-1}) was found in T_9 (Banana) whereas samples from T_7 (Apple) showed lowest Ni concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Ni in sampled fruits under consideration of health risk given by FAO/WHO is 0.80 mg kg^{-1} (Table 3.1) which is higher than Ni content in collected fruit samples. So, according to FAO/WHO (2011), Ni content in collected fruit samples from Agora super market of Dhanmondi, Dhaka might not be risk for health in terms of over Ni content.

Table 4.2. Heavy metal concentration in collected fruit samples from Agora super market of Dhanmondi in Dhaka city

Treatment	Heavy metal concentration in fruit samples (mg/kg) collected from Agora super market, Dhanmondi, Dhaka				
	Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)
T_6 (Grape)	0.06 c	0.002	0.003	0.002	0.003
T_7 (Apple)	0.03 c	0.004	0.003	0.001	0.002
T_8 (Orange)	0.02 c	0.002	0.002	0.003	0.002
T_9 (Banana)	0.21 a	0.004	0.006	0.004	0.001
T_{10} (Pomegranate)	0.11 b	0.001	0.002	0.002	0.002
$LSD_{0.05}$	0.083	NS	NS	NS	NS
CV(%)	2.88	2.64	2.07	1.73	1.92
MAC (FAO/WHO, 2011)	1.50	0.20	2.30	0.80	50.00

*MAC = Maximum allowable concentration

Consideration of Co (Cobalt) concentration, it is ranged from 0.001 to 0.003 mg kg^{-1} among the fruit samples. Results indicated that the highest Co concentration (0.003 mg kg^{-1}) was found in T_6 (Grape) whereas samples from T_9 (Banana) showed lowest Co concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Co in sampled fruits under consideration of health risk given by FAO/WHO is 50.00 mg kg^{-1} (Table 4.2) which is higher than Co content in collected fruit samples. So, according to FAO/WHO (2011), Co content in collected fruit samples from Agora super market of Dhanmondi, Dhaka might not be risk for health in terms of over Co content.

4.3 Heavy metals in fruit samples collected from Agora super market

Table 4.3 shows different fruit samples collected from Prince Bazar of Mirpur-1, Dhaka containing different detected heavy metal. Total fifteen samples of different fruits (three samples of each of five fruits *viz*. Grape, Apple, Orange, Banana and Pomegranate) were analyzed to find out the heavy metal contamination (Pb, Cd, Cr, Ni and Co).

Significant variation was found in terms of Pb concentration in different fruit samples but non-significant variation was observed in terms of Cd, Cr, Ni and Co concentration in different fruit samples collected from Prince Bazar of Mirpur-1, Dhaka (Table 4.3 and Appendix III).

Regarding Pb (Lead) concentration, it is ranged from 0.03 to 0.18 mg kg^{-1} among the fruit samples. Results indicated that the highest Pb concentration (0.18 mg kg^{-1}) was found in T_{14} (Banana) which was statistically similar with T_{12} (Apple) and T_{15} (Pomegranate). Again, the sample from T_{11} (Grape) showed lowest Pb concentration (0.03 mg kg^{-1}) which was significantly same with T_{13} (Orange). Maximum allowable concentration of Pb in sampled fruits under consideration of health risk given by FAO/WHO is 1.50 mg kg^{-1} (Table 4.3) which is higher than Pb content in collected fruit samples. So, according to FAO/WHO (2011), Pb content in collected fruit samples from Prince Bazar of Mirpur-1, Dhaka might not be risk for health in terms of over Pb content.

Consideration of Cd (Cadmium) concentration, it is ranged from 0.002 to 0.011 mg kg^{-1} among the fruit samples. Results indicated that the highest Cd concentration (0.011 mg kg^{-1}) was found in T_{14} (Banana) whereas samples from T_{15} (Pomegranate) showed lowest Cd concentration (0.002 mg kg^{-1}). Maximum allowable concentration of Cd in sampled fruits under consideration of health risk given by FAO/WHO is 0.20 mg kg^{-1} (Table 4.3) which is higher than Cd content in collected fruit samples. So, according to FAO/WHO (2011), Cd content in collected fruit samples from Prince Bazar of Mirpur-1, Dhaka may not be risk for health in terms of over Cd content.

Table 4.3. Heavy metal concentration in collected fruit samples from Prince Bazar of Mirpur-1 in Dhaka city

Treatment	Heavy metal concentration in fruit samples (mg/kg) collected from Prince Bazar, Mirpur 1, Dhaka				
	Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)
T_{11} (Grape)	0.03 c	0.003	0.001	0.002	0.003
T_{12} (Apple)	0.12 ab	0.006	0.004	0.004	0.004
T_{13} (Orange)	0.04 c	0.005	0.002	0.001	0.003
T_{14} (Banana)	0.18 a	0.011	0.003	0.007	0.003
T_{15} (Pomegranate)	0.14 ab	0.002	0.005	0.002	0.002
$LSD_{0.05}$	0.076	NS	NS	NS	NS
CV(%)	3.09	2.56	1.76	1.87	1.44
MAC (FAO/WHO, 2011)	1.50	0.20	2.30	0.80	50.00

*MAC = Maximum allowable concentration

In case of Cr (Chromium) concentration, it is ranged from 0.001 to 0.005 mg kg^{-1} among the fruit samples. Results indicated that the highest Cr concentration (0.005 mg kg^{-1}) was found in T_{15} (Pomegranate) whereas samples from T_{11} (Grape) showed lowest Cr concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Cr in sampled fruits under consideration of health risk given by FAO/WHO is 2.30 mg kg^{-1} (Table 4.3) which is higher than Cr content in collected fruit samples. So, according to FAO/WHO (2011), Cr content in collected fruit samples from Prince Bazar of Mirpur-1, Dhaka might not be risk for health in terms of over Cr content.

In terms of Ni (Nickel) concentration, it is ranged from 0.001 to 0.007 mg kg^{-1} among the fruit samples. Results indicated that the highest Ni concentration (0.007 mg kg^{-1}) was found in T_{14} (Banana) whereas samples from T_{13} (Orange) showed lowest Ni concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Ni in sampled fruits under consideration of health risk given by FAO/WHO is 0.80 mg kg^{-1} (Table 4.3) which is higher than Ni content in collected fruit samples. So, according to FAO/WHO (2011), Ni content in collected fruit samples from Prince Bazar of Mirpur-1, Dhaka might not be risk for health in terms of over Ni content.

Consideration of Co (Cobalt) concentration, it is ranged from 0.002 to 0.004 mg kg^{-1} among the fruit samples. Results indicated that the highest Co concentration (0.004 mg kg^{-1}) was found in T_{12} (Apple) whereas samples from T_{15} (Pomegranate) showed lowest Co concentration (0.002 mg kg^{-1}). Maximum allowable concentration of Co in sampled fruits under consideration of health risk given by FAO/WHO is 50.00 mg kg^{-1} (Table 4.3) which is higher than Co content in collected fruit samples. So, according to FAO/WHO (2011), Co content in collected fruit samples from Prince Bazar of Mirpur-1, Dhaka might not be risk for health in terms of over Co content.

4.4 Heavy metals in fruit samples collected from Kawran Bazar fruit market

Table 4.4 shows different fruit samples collected from Kawran Bazar fruit market of Kawran Bazar, Dhaka containing different detected heavy metal. Total fifteen samples of different fruits (three samples of each of five fruits *viz.* Grape, Apple, Orange, Banana and Pomegranate) were analyzed to find out the heavy metal contamination (Pb, Cd, Cr, Ni and Co).

Significant variation was found in terms of Pb concentration in different fruit samples but non-significant variation was observed in terms of Cd, Cr, Ni and Co concentration in different fruit samples collected from Kawran Bazar fruit market of Kawran Bazar, Dhaka (Table 4.4 and Appendix IV).

Regarding Pb (Lead) concentration, it is ranged from 0.03 to 1.31 mg kg^{-1} among the fruit samples. Results indicated that the highest Pb concentration (1.31 mg kg^{-1}) was found in T_{19} (Banana) which was significantly different from other samples. Again, the sample from T_{18} (Orange) showed lowest Pb concentration (0.03 mg kg^{-1}) which was significantly same with T_{16} (Grape) and T_{17} (Apple). Maximum allowable concentration of Pb in sampled fruits under consideration of health risk given by FAO/WHO is 1.50 mg kg^{-1} (Table 4.4) which is higher than Pb content in collected fruit samples. So, according to FAO/WHO (2011), Pb content in collected fruit samples from Kawran Bazar fruit market of Kawran Bazar, Dhaka might not be risk for health in terms of over Pb content.

Consideration of Cd (Cadmium) concentration, it is ranged from 0.001 to 0.004 mg kg^{-1} among the fruit samples. Results indicated that the highest Cd concentration (0.004 mg kg^{-1}) was found in T_{17} (Apple) and T_{18} (Orange) whereas samples from T_{19} (Banana) showed lowest Cd concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Cd in sampled fruits under consideration of health risk given by FAO/WHO is 0.20 mg kg^{-1} (Table 4.4) which is higher than Cd content in collected fruit samples. So, according to FAO/WHO (2011), Cd content in collected fruit samples from Kawran Bazar fruit market of Kawran Bazar, Dhaka may not be risk for health in terms of over Cd content.

In case of Cr (Chromium) concentration, it is ranged from 0.002 to 0.004 mg kg^{-1} among the fruit samples. Results indicated that the highest Cr concentration (0.004 mg kg^{-1}) was found in T_{19} (Banana) whereas samples from T_{18} (Orange) and T_{20} (Pomegranate) showed lowest Cr concentration

(0.002 mg kg^{-1}). Maximum allowable concentration of Cr in sampled fruits under consideration of health risk given by FAO/WHO is 2.30 mg kg^{-1} (Table 4.4) which is higher than Cr content in collected fruit samples. So, according to FAO/WHO (2011), Cr content in collected fruit samples from Kawran Bazar fruit market of Kawran Bazar, Dhaka might not be risk for health in terms of over Cr content.

In terms of Ni (Nickel) concentration, it is ranged from 0.002 to 0.016 mg kg^{-1} among the fruit samples. Results indicated that the highest Ni concentration (0.016 mg kg^{-1}) was found in T_{19} (Banana) followed by T_{17} (Apple) whereas samples from T_{18} (Orange) showed lowest Ni concentration (0.002 mg kg^{-1}). Maximum allowable concentration of Ni in sampled fruits under consideration of health risk given by FAO/WHO is 0.80 mg kg^{-1} (Table 4.4) which is higher than Ni content in collected fruit samples. So, according to FAO/WHO (2011), Ni content in collected fruit samples from Kawran Bazar fruit market of Kawran Bazar, Dhaka might not be risk for health in terms of over Ni content.

Consideration of Co (Cobalt) concentration, it is ranged from 0.001 to 0.003 mg kg^{-1} among the fruit samples. Results indicated that the highest Co concentration (0.003 mg kg^{-1}) was found in T_{17} (Apple) whereas samples from T_{20} (Pomegranate) showed lowest Co concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Co in sampled fruits under consideration of health risk given by FAO/WHO is 50.00 mg kg^{-1} (Table 4.4) which is higher than Co content in collected fruit samples. So, according to FAO/WHO (2011), Co content in collected fruit samples from Kawran Bazar fruit market of Kawran Bazar, Dhaka might not be risk for health in terms of over Co content.

Table 4.4. Heavy metal concentration in collected fruit samples from Kawran Bazar fruit market of Kawran Bazar in Dhaka city

Treatment	Heavy metal concentration in fruit samples (mg/kg) collected from Kawran Bazar fruit market, Kawran Bazar, Dhaka				
	Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)
T_{16} (Grape)	0.07 c	0.002	0.003	0.003	0.002
T_{17} (Apple)	0.11 c	0.004	0.003	0.011	0.003
T_{18} (Orange)	0.03 c	0.004	0.002	0.002	0.002
T_{19} (Banana)	1.31 a	0.001	0.004	0.016	0.002
T_{20} (Pomegranate)	0.42 b	0.003	0.002	0.004	0.001
$LSD_{0.05}$	0.106	NS	NS	NS	NS
CV(%)	3.36	1.52	2.17	1.33	1.24
MAC (FAO/WHO, 2011)	1.50	0.20	2.30	0.80	50.00

*MAC = Maximum allowable concentration

4.5 Heavy metals in fruit samples collected from Meena Bazar of Shyamoli

Table 4.5 shows different fruit samples collected from Meena Bazar of Shyamoli, Dhaka containing different detected heavy metal. Total fifteen samples of different fruits (three samples of each of five fruits *viz*. Grape, Apple, Orange, Banana and Pomegranate) were analyzed to find out the heavy metal contamination (Pb, Cd, Cr, Ni and Co).

Significant variation was found in terms of Pb concentration in different fruit samples but non-significant variation was observed in terms of Cd, Cr, Ni and Co concentration in different fruit samples collected from Meena Bazar of Shyamoli, Dhaka (Table 4.5 and Appendix V).

Regarding Pb (Lead) concentration, it is ranged from 0.04 to 1.24 mg kg^{-1} among the fruit samples. Results indicated that the highest Pb concentration (1.24 mg kg^{-1}) was found in T_{24} (Banana) which was statistically different from other treatments. Again, the sample from T_{23} (Orange) showed lowest Pb concentration (0.04 mg kg^{-1}) which was significantly same with T_{22} (Apple) and T_{25} (Pomegranate). Maximum allowable concentration of Pb in sampled fruits under consideration of health risk given by FAO/WHO is 1.50 mg kg^{-1} (Table 4.5) which is higher than Pb content in collected fruit samples. So, according to FAO/WHO (2011), Pb content in collected fruit samples from Meena Bazar of Shyamoli, Dhaka might not be risk for health in terms of over Pb content.

Consideration of Cd (Cadmium) concentration, it is ranged from 0.002 to 0.008 mg kg^{-1} among the fruit samples. Results indicated that the highest Cd concentration (0.008 mg kg^{-1}) was found in T_{24} (Banana) whereas samples from T_{25} (Pomegranate) showed lowest Cd concentration (0.002 mg kg^{-1}). Maximum allowable concentration of Cd in sampled fruits under consideration of health risk given by FAO/WHO is 0.20 mg kg^{-1} (Table 4.5) which is higher than Cd content in collected fruit samples. So, according to FAO/WHO (2011), Cd content in collected fruit samples from Meena Bazar of Shyamoli, Dhaka may not be risk for health in terms of over Cd content.

In case of Cr (Chromium) concentration, it is ranged from 0.001 to 0.004 mg kg^{-1} among the fruit samples. Results indicated that the highest Cr concentration (0.004 mg kg^{-1}) was found in T_{21} (Grape) whereas samples from T_{22} (Apple) showed lowest Cr concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Cr in sampled fruits under consideration of health risk given by FAO/WHO is 2.30 mg kg^{-1} (Table 4.5) which is higher than Cr content in collected fruit samples. So, according to FAO/WHO (2011), Cr content in collected fruit samples from Meena Bazar of Shyamoli, Dhaka might not be risk for health in terms of over Cr content.

In terms of Ni (Nickel) concentration, it is ranged from 0.001 to 0.004 mg kg^{-1} among the fruit samples. Results indicated that the highest Ni concentration (0.004 mg kg^{-1}) was found in T_{24} (Banana) whereas samples from T_{25}

(Pomegranate) showed lowest Ni concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Ni in sampled fruits under consideration of health risk given by FAO/WHO is 0.80 mg kg^{-1} (Table 4.5) which is higher than Ni content in collected fruit samples. So, according to FAO/WHO (2011), Ni content in collected fruit samples from Meena Bazar of Shyamoli, Dhaka might not be risk for health in terms of over Ni content.

Consideration of Co (Cobalt) concentration, it is ranged from 0.001 to 0.003 mg kg^{-1} among the fruit samples. Results indicated that the highest Co concentration (0.003 mg kg^{-1}) was found in T_{22} (Apple), T_{23} (Orange) and T_{24} (Banana) whereas samples from T_{21} (Grape) and T_{25} (Pomegranate) showed lowest Co concentration (0.001 mg kg^{-1}). Maximum allowable concentration of Co in sampled fruits under consideration of health risk given by FAO/WHO is 50.00 mg kg^{-1} (Table 4.5) which is higher than Co content in collected fruit samples. So, according to FAO/WHO (2011), Co content in collected fruit samples from Meena Bazar of Shyamoli, Dhaka might not be risk for health in terms of over Co content.

Table 4.5. Heavy metal concentration in collected fruit samples from Meena Bazar of Shyamoli in Dhaka city

Treatment	Heavy metal concentration in fruit samples (mg/kg) collected from Meena Bazar, Shyamoli, Dhaka				
	Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)
T_{21} (Grape)	0.16 b	0.006	0.004	0.002	0.001
T_{22} (Apple)	0.07 c	0.003	0.001	0.003	0.003
T_{23} (Orange)	0.04 c	0.004	0.003	0.002	0.003
T_{24} (Banana)	1.24 a	0.008	0.002	0.004	0.003
T_{25} (Pomegranate)	0.06 c	0.002	0.003	0.001	0.001
$LSD_{0.05}$	0.084	NS	NS	NS	NS
CV(%)	2.97	2.14	1.52	2.03	1.36
MAC (FAO/WHO, 2011)	1.50	0.20	2.30	0.80	50.00

*MAC = Maximum allowable concentration

Heavy metal pollution has spread broadly over the globe, perturbing the environment and posing serious health hazards to humans. The root causes of this problem are generally held to be the rapid pace of urbanization, land use changes, and industrialization, especially in developing countries with extremely high populations, such as India, China and Bangladwsh (UN-HABITAT, 2004). Several hazardous heavy metals and metalloids (e.g., Pb, Cd, Cr, As, Co, Ni and Hg) are classified as non-essential to metabolic and other biological functions. Those metals are deleterious in various respects (Gall *et al*., 2015), and they have therefore been included in the top 20 list of dangerous substances by the United States Environmental Protection Agency and the Agency for Toxic Substances and Disease Registry (ATSDR) (ATSDR, 2007; Xiong *et al*., 2016a, 2016b; Khalid *et al*., 2017; Rai, 2018).

Food safety is major issue of concern due to increasing concentrations of heavy metals and other industrial environmental contaminants (Arisseto-Bragotto, 2017). Heavy metals (e.g., Pb, Cd, Co, Cr and Ni) in food crops were reported to impose human health hazards (Rodriguez, 2014; Blanco, 2017).

The ingestion of fruits and vegetables contaminated with heavy metals causes serious human health issues, such as gastrointestinal cancer, fragile immunological mechanisms, mental growth retardation, and malnutrition (Hu *et al*., 2013; Gress *et al*., 2015; Dickin *et al*., 2016; El-Kady and Abdel-Wahhab, 2018).

Several works have been done on heavy metal contents (eg. Pb, Cd, Cr, Ni and Co) in fruits which showed different concentrations which are below the permissible limit according to FAO/WHO in most of the cases. Mahdavian and Somashekar (2009) determined lead, zinc, cadmium, copper, cobalt, chromium, iron, manganese and nickel in different fruits *viz*. grape, pomegranate, orange, banana, lemon, pear, apple, sapota, mango and guava and found safe ranges of heavy metal contamination regarding FAO/WHO (2011). Similar result was also found by Verma *et al*. (2016), Ezigbo and Obiageli (2015), Sajib *et al*. (2014, Ghosh *et al*. (2011) and Sobukola *et al*. (2010).

Human health hazards are closely linked to the intake of metal-contaminated food crops. Heavy metals can accumulate in human bones or fatty tissues through dietary intake, thereby leading to the depletion of essential nutrients and weakened immunological defenses. Certain heavy metals (e.g., Al, Cd, Mn, Pb, Cr, Co, As and Ni) are further suspected to cause intrauterine growth retardation (Khan *et al*., 2010; Rai, 2018). Lead contamination adversely affects mental growth, causing neurological and cardiovascular diseases in humans, especially children (Zhou, 2016; Al-Saleh *et al*., 2017). Certain heavy metals, especially Pb and Cd, have carcinogenic effects (Trichopoulos, 1997) and can also lead to bone fractures and malformation, cardiovascular complications, kidney dysfunction, hypertension, and other serious diseases of the liver, lung, nervous system, and immune system (Zhou, 2016; El-Kady and Abdel-Wahhab, 2018). Chromium compounds, such as calcium chromate, zinc chromates, strontium chromate and lead chromates, are highly toxic and carcinogenic in nature. Common features due to Cr phytotoxicity are reduction in root growth, leaf chlorosis, inhibition of seed germination and depressed biomass. Chromium toxicity causes chlorosis and necrosis in plants (Ghani, 2011). Basu *et al*. (2010) and Ryuko *et al*. (2012) report that the most frequent symptoms of cobalt excess are skin inflammations and asthma.

The exposure of consumers and the related health risks are usually expressed in terms of the provisional tolerable daily intake (PTDI) (FAO/WHO, 1999). The FAO/WHO have set a limit for the heavy metal intake based on body weight for an average adult, namely, 60 kg body weight. The average diets per person per day of fruits are 98 and 78 g, respectively. According to FAO/WHO (2011), the highest permissible limit of heavy metal like Pb, Cd, Cr, Ni and Co is 1.50, 0.20, 2.30, 0.80 and 50.00 mg kg^{-1}, respectively and if intake of heavy metal through fruit consumption is safe for human body.

4.6 Single factor pollution index (PI)

Pollution index (PI) is an important factor for the determination of pollution in the collected fruit samples from different places of Dhaka city. Value of PI<1 indicates that the collected samples are not yet contaminated, whereas PI>1 indicates pollution. Similarly, PI=1 indicates a critical state which makes the involved samples useful for environmental monitoring (Chukwuma, 1994).

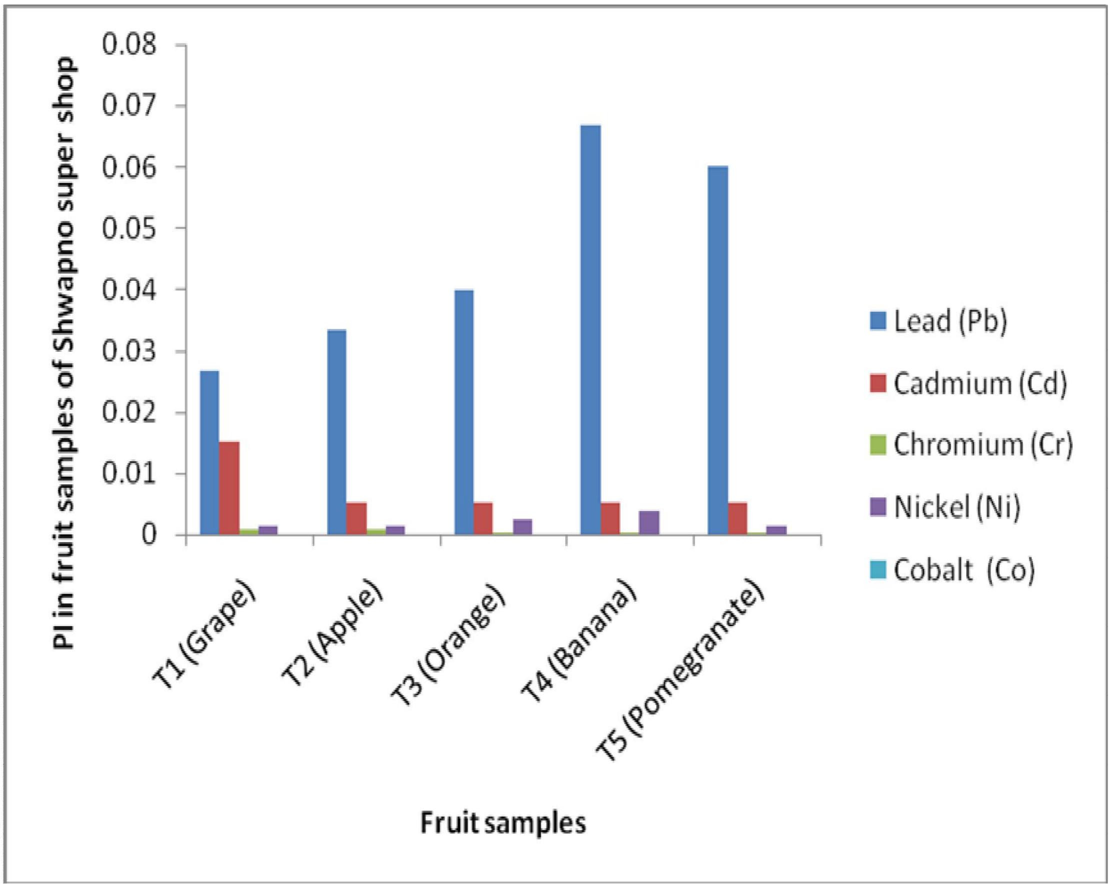

Figure 4.1 Single factor pollution index (PI) in fruit samples collected Shwapno super shop, Mirpur-10, Dhaka

In terms of collected fruit samples from Shwapno super shop, Mirpur-10, Dhaka, are not yet contaminated (PI<1) in terms of Pb, Cd, Cr, Ni and Co contamination (Figure 4.1). So, selected fruit collection in this shop is safe for the environment as well as health.

In terms of collected fruit samples from Agora super market of Dhanmondi, Dhaka, are not yet contaminated (PI<1) in terms of Pb, Cd, Cr, Ni and Co contamination (Figure 4.2). So, selected fruit collection in this shop is safe for the environment as well as health.

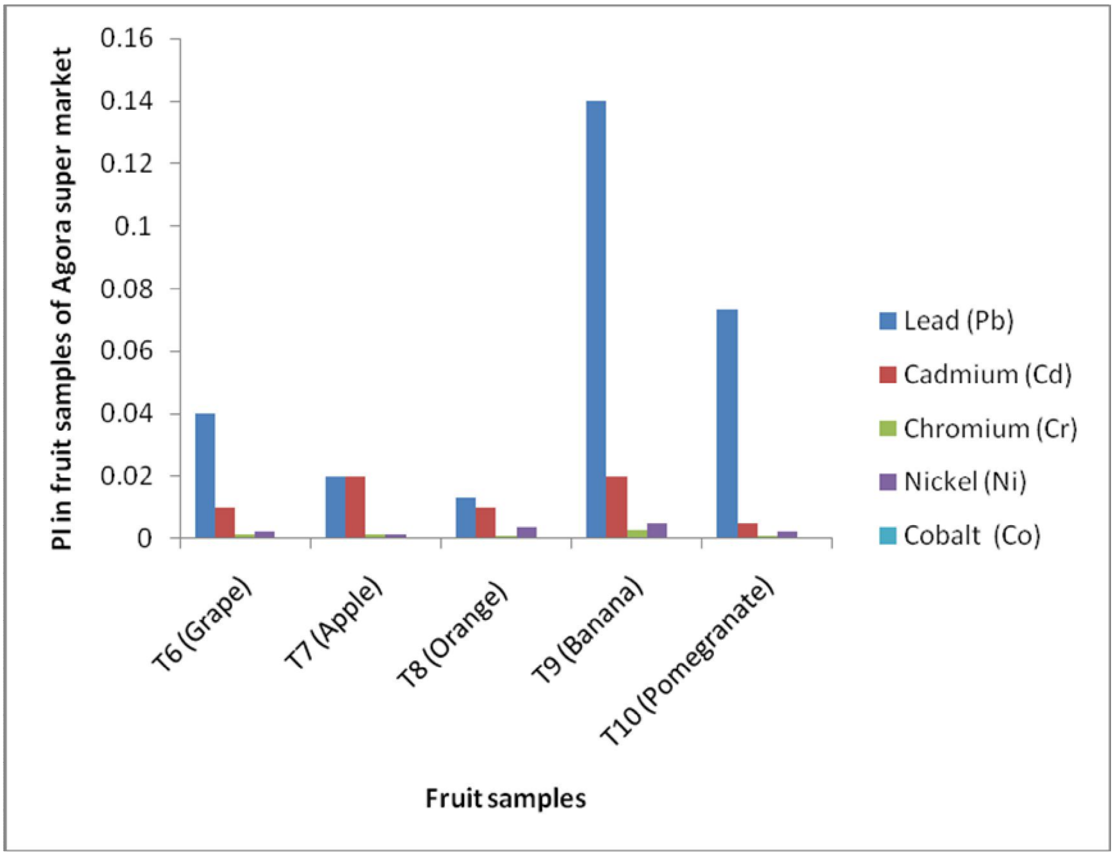

Figure 4.2 Single factor pollution index (PI) in fruit samples collected from Agora super market of Dhanmondi, Dhaka

In terms of collected fruit samples from Prince Bazar of Mirpur-1, Dhaka, are not yet contaminated (PI<1) in terms of Pb, Cd, Cr, Ni and Co contamination (Figure 4.3). So, selected fruit collection in this shop is safe for the environment as well as health.

In terms of collected fruit samples from Kawran Bazar fruit market of Kawran Bazar, Dhaka, are not yet contaminated (PI<1) in terms of Pb, Cd, Cr, Ni and Co contamination (Figure 4.4). So, selected fruit collection in this shop is safe for the environment as well as health.

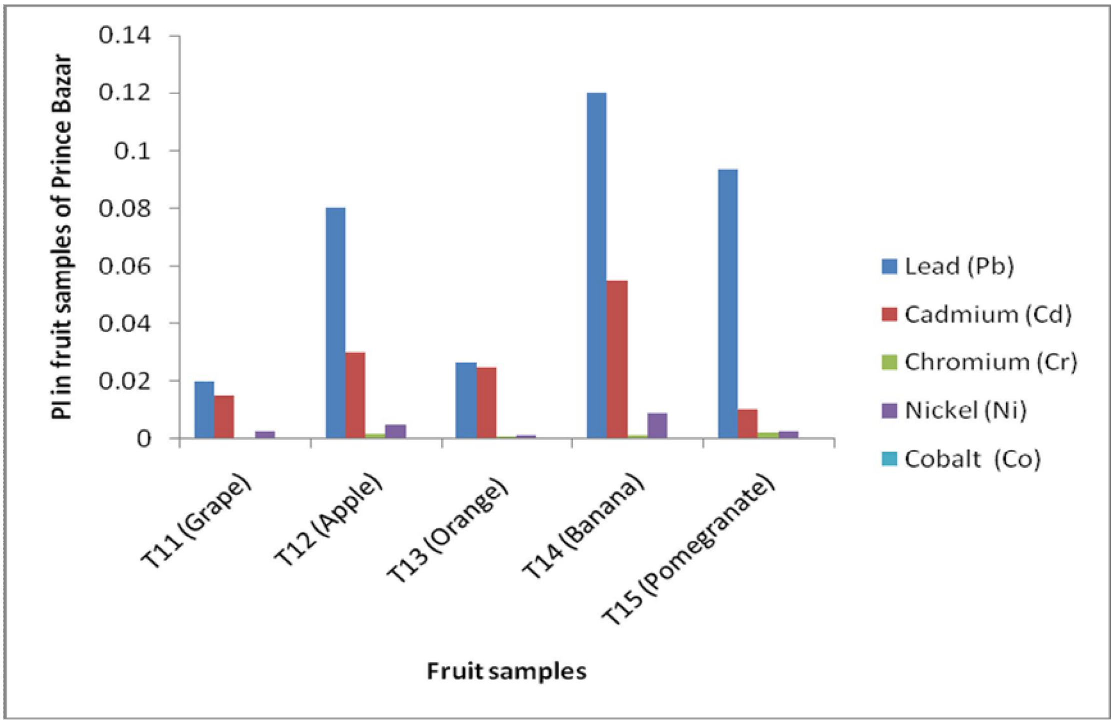

Figure 4.3 Single factor pollution index (PI) in fruit samples collected from Prince Bazar of Mirpur-1, Dhaka

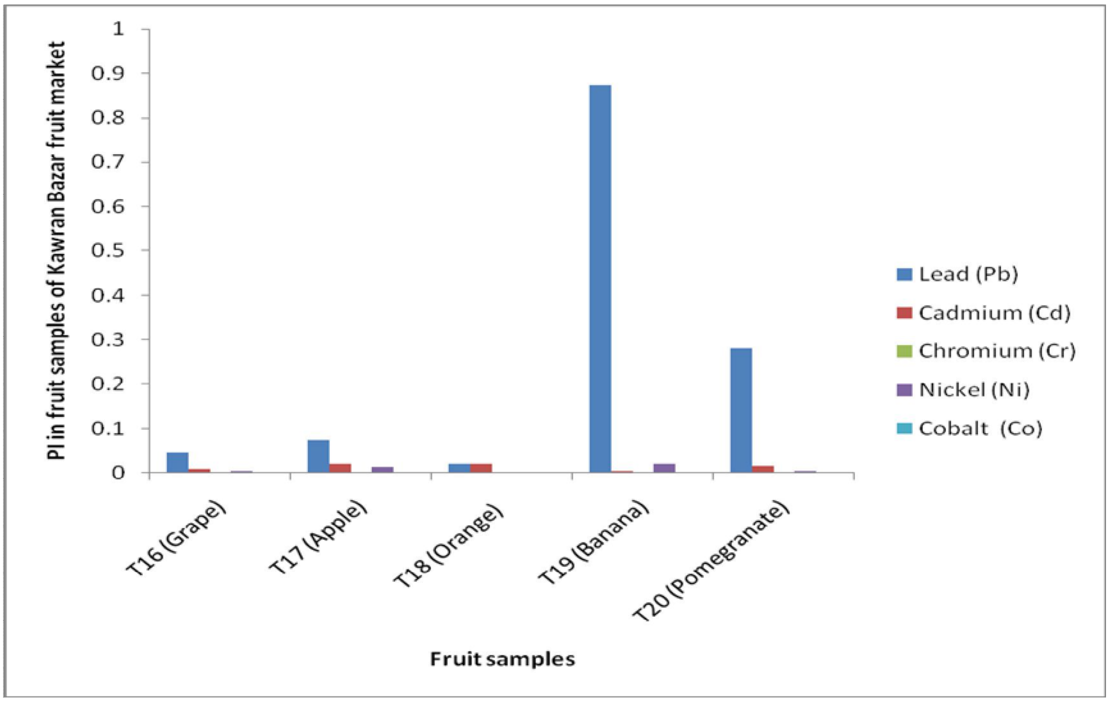

Figure 4.4 Single factor pollution index (PI) in fruit samples collected from from Kawran Bazar fruit market of Kawran Bazar, Dhaka

In terms of collected fruit samples from Meena Bazar of Shyamoli, Dhaka, are not yet contaminated (PI<1) in terms of Pb, Cd, Cr, Ni and Co contamination (Figure 4.5). So, selected fruit collection in this shop is safe for the environment as well as health.

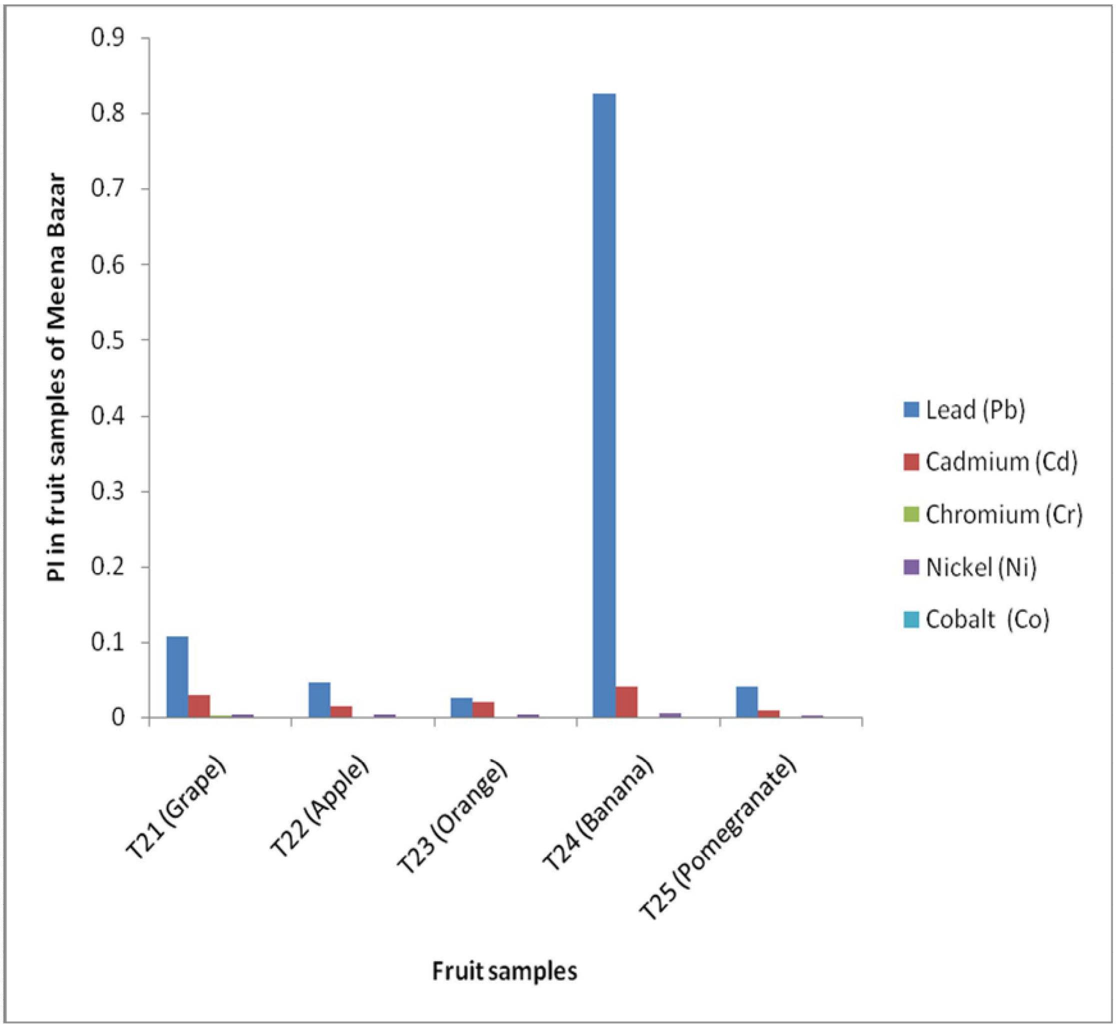

Figure 4.5 Single factor pollution index (PI) in fruit samples collected from Meena Bazar of Shyamoli, Dhaka

4.7 Sum of pollution index (SPI)

Sum of pollution index (SPI) showed little variation in different collected fruit amples from different places of Dhaka city (Figure 4.6). Results showed that the highest SPI (0.9001) was in Banana found in Kawran Bazar fruit market of Kawran Bazar, Dhaka area (T_{19}) followed by Meena Bazar of Shyamoli, Dhaka

(0.8726) in Banana (T_{24}) whereas the lowest SPI (0.028) was in Orange found in Agora super market of Dhanmondi, Dhaka (T_8) followed by Prince Bazar of Mirpur-1, Dhaka (0.038) in Grape (T_{11}).

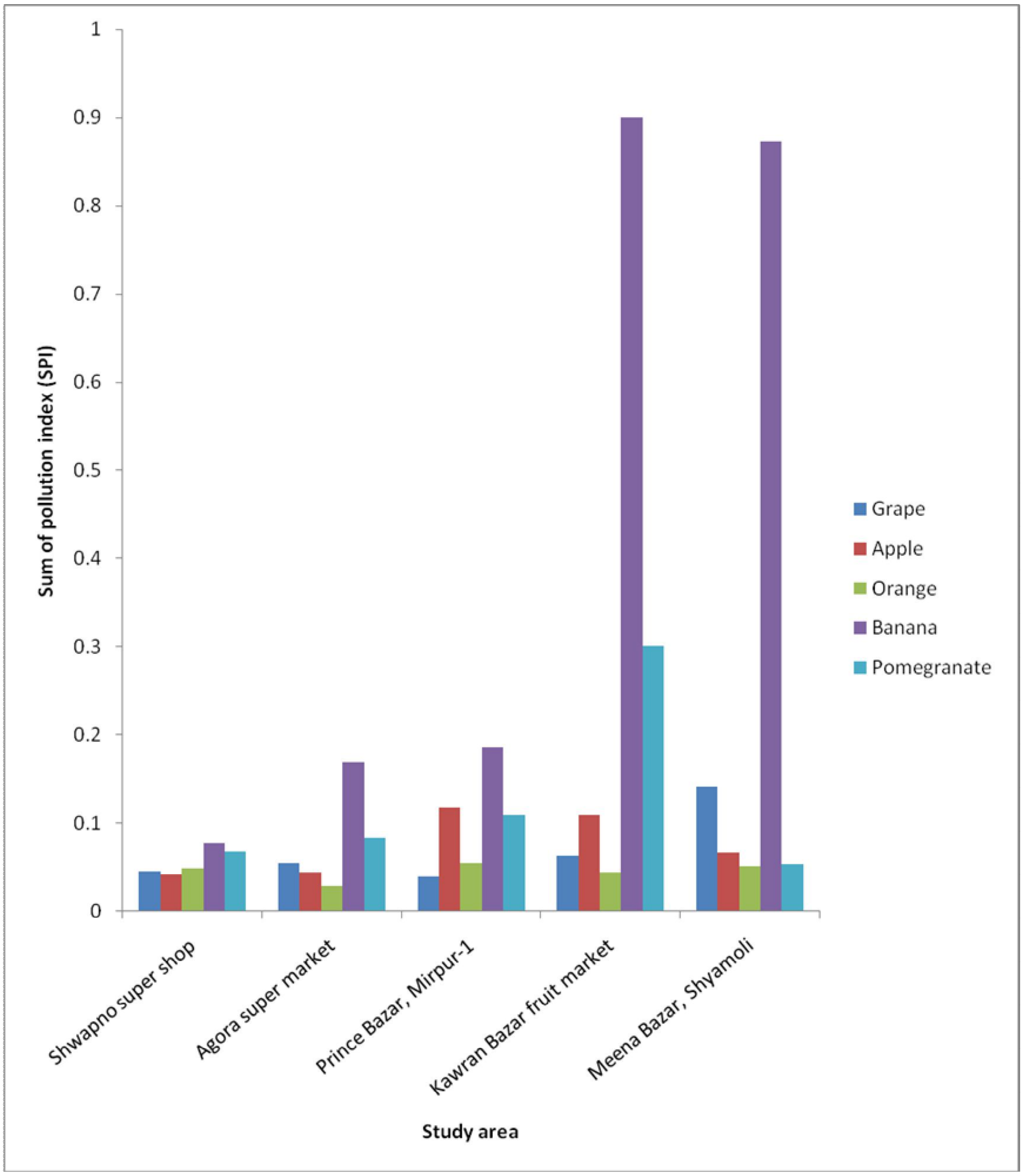

Figure 4.6 Sum of pollution index (SPI) in selected fruit samples in the study area

4.8 Metal pollution index (MPI)

Figure 4.7 showed that the highest MPI (0.0119) was in Banana found in Meena Bazar of Shyamoli, Dhaka whereas the lowest MPI (0.0025) was in Pomegranate found in Shwapno super shop, Mirpur-10, Dhaka.

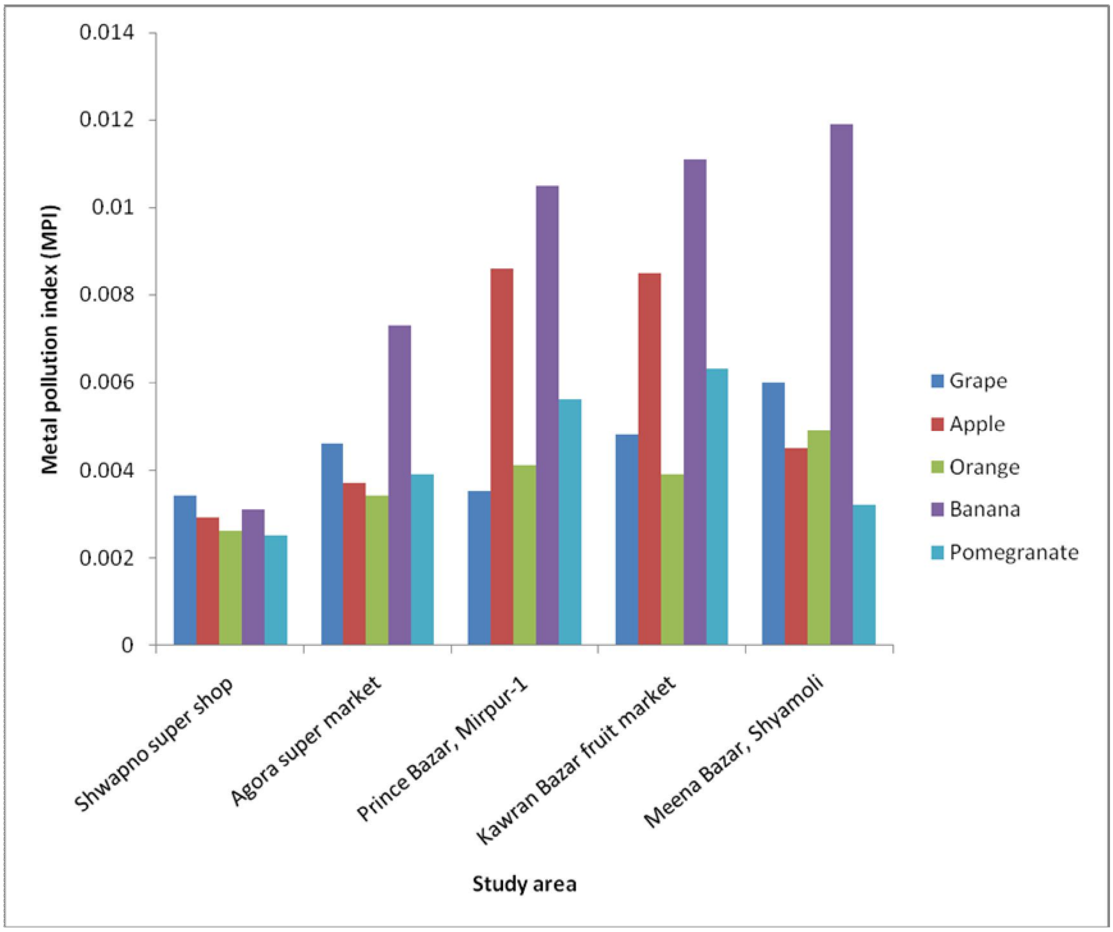

Figure 4.7 Metal pollution index (MPI) in soil, water, rice grain and rice straw in the study area

CHAPTER V

SUMMARY AND CONCLUSION

The study was carried out at the Agricultural Chemistry Department Laboratory of Sher-e-Bangla Agricultural University, Sher-e-Bangla Nagar, Dhaka, during the season 2018-19 for the determination and risk analysis of heavy metals in different fruits collected from different shops of Dhaka city. Five (5) places *viz*. (1) Shwapno super shop of Mirpur-10, Dhaka, (2) Agora super market, Dhanmondi, Dhaka, (3) Prince Bazar, Mirpur-1, Dhaka, (4) Kawran Bazar fruit market, Kawran Bazar, Dhaka and (5) Meena Bazar, Shyamoli, Dhaka were selected for sample collection. Samples were collected on five fruits namely (i) Grape, (ii) Apple, (iii) Orange, (iv) Banana and (v) Pomegranate. So, twenty five unit samples were considered for the present study which was replicated thrice and remarked as T_1 to T_{25}. The experiment was laid out in Completely Randomized Design (CRD). Samples were analyzed to determine lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni) and cobalt (Co) using atomic absorption spectroscopy analysis. Single factor pollution index (PI), sum of pollution index (SPI) and metal pollution index (MPI) were also determined from collected data.

Considering different fruit samples collected from Shwapno super shop of Mirpur-10, Dhaka, the highest Pb and Ni (0.10 and 0.003 mg kg^{-1}, respectively) was found in T_4 (Banana) sample but the highest Cd concentration (0.003 mg kg^{-1}) was found in T_1 (Grape). Again, the highest Cr and Co concentration (0.002 and 0.002 mg kg^{-1}, respectively) were found in T_1 (Grape) and T_2 (Apple) samples. Similarly, T_1 (Grape) sample showed lowest Pb concentration (0.04 mg kg^{-1}) whereas the showed lowest Cd and Cr concentration (0.001 mg kg^{-1}, respectively) was found from T_2 (Apple), T_3 (Orange) and T_4 (Banana) samples. Again, T_3 (Orange), T_4 (Banana) and T_5 (Pomegranate) samples showed lowest Co concentration (0.001 mg kg^{-1})

whereas T_1 (Grape), T_2 (Apple) and T_5 (Pomegranate) showed lowest Ni concentration (0.001 mg kg^{-1}).

In terms of different fruit samples collected from Agora super market, Dhanmondi, Dhaka, the highest Pb, Cr and Ni concentration, (0.21, 0.006 and 0.004 mg kg^{-1}, respectively) were found in T_9 (Banana) sample whereas the highest Cd concentration (0.004 mg kg^{-1}) was found in T_7 (Apple) and T_9 (Banana) samples and highest Co concentration (0.003 mg kg^{-1}) was found in T_6 (Grape) sample. Similarly, T_8 (Orange), T_7 (Apple) and T_9 (Banana) samples respectively showed lowest Pb, Ni and Co concentration (0.02, 0.001 and 0.001 mg kg^{-1}, respectively) whereas T_{10} (Pomegranate) sample showed lowest Cd and Cr concentration (0.001 and 0.002 mg kg^{-1}, respectively).

Regarding different fruit samples collected from Prince Bazar, Mirpur-1, Dhaka, The highest Pb, Cd and Ni concentration (0.18, 0.011 and 0.007 mg kg^{-1}, respectively) were found in T_{14} (Banana) sample whereas the highest Cr and Co concentration (0.005 and 0.004 mg kg^{-1}, respectively) was found in T_{15} (Pomegranate) and T_{12} (Apple) samples, respectively. Similarly, the T_{11} (Grape) sample showed lowest Pb and Cr concentration (0.03 and 0.001 mg kg^{-1}, respectively) whereas T_{15} (Pomegranate) sample showed lowest Cd and Co concentration (0.002 mg kg^{-1}, respectively) but T_{13} (Orange) sample showed lowest Ni concentration (0.001 mg kg^{-1}).

Regarding different fruit samples collected from Kawran Bazar fruit market, Kawran Bazar, Dhaka the highest Pb, Cr and Ni concentration (1.31, 0.004 and 0.016 mg kg^{-1}) was found in T_{19} (Banana) sample whereas the highest Cd concentration (0.004 mg kg^{-1}) was found in T_{17} (Apple) and T_{18} (Orange) samples but the highest Co concentration (0.003 mg kg^{-1}) was found in T_{20} (Pomegranate) sample. Similarly, T_{18} (Orange) sample showed lowest Pb and Ni concentration (0.03 and 0.002 mg kg^{-1}, respectively) whereas T_{16} (Grape), T_{18} (Orange) and T_{19} (Banana) sample s showed lowest Co concentration (0.001 mg kg^{-1}). Again, T_{19} (Banana) sample and showed lowest Cd concentration (0.001 mg kg^{-1}) and T_{18} (Orange) and T_{20} (Pomegranate) samples showed lowest Cr concentration (0.002 mg kg^{-1})

In terms of different fruit samples collected from Meena Bazar, Shyamoli, Dhaka the highest Pb, Cd and Ni concentration (1.24, 0.008 and 0.004 mg kg^{-1}, respectively) was found in T_{24} (Banana) sample whereas the highest Cr concentration (0.004 mg kg^{-1}) was found in T_{21} (Grape) sample and highest Co concentration (0.003 mg kg^{-1}) was found in T_{21} (Grape) and T_{25} (Pomegranate) samples. Similarly, T_{23} (Orange) sample showed lowest Pb concentration (0.04 mg kg^{-1}) but T_{25} (Pomegranate) sample showed lowest Cd and Ni concentration (0.002 and 0.001 mg kg^{-1}, respectively). Again, T_{22} (Apple) sample showed lowest Cr concentration (0.001 mg kg^{-1}) but T_{22} (Apple), T_{23} (Orange) and T_{24} (Banana) samples showed lowest Co concentration (0.001 mg kg^{-1}).

Regarding Pollution index (PI), all collected samples from selected areas of Dhaka city was in $PI<1$ which indicates that the collected samples are not yet contaminated in respect of heavy metal content. In case of Sum of pollution index (SPI), the highest SPI (0.9001) was in Banana found in Kawran Bazar fruit market of Kawran Bazar, Dhaka whereas the lowest SPI (0.028) was in Orange found in Agora super market of Dhanmondi, Dhaka. Again, considering, Metal pollution index (MPI), the highest MPI (0.0119) was in Banana found in Meena Bazar of Shyamoli, Dhaka whereas the lowest MPI (0.0025) was in Pomegranate found in Shwapno super shop, Mirpur-10, Dhaka.

From the above results, it can be concluded that heavy metals contamination in the study areas in terms of Pb, Cd, Cr, Ni and Co were in little variation and the heavy metals in collected fruit samples were below safe limit approved by FAO/WHO.

Recommendation

From the above result, therefore, reported that heavy metals in fruit samples of the study area was below safe limit approved by FAO/WHO. So, further study can be conducted in other areas of Bangladesh to justify the present study.

REFERENCES

Adeleken, B. and Abegunde, K. (2011). Heavy metal contamination of soil and ground water at automobile mechanic village in Ibadan, Nigeria. *Int. J. Physic. Sci*. **6**: 1045-1058.

Agbenin, J.O. (2009): The impact of long-term cultivation and management history on the status and dynamics of cobalt in a savanna Alfisol in Nigeria. *European J. Soil Sci*. **53**(2): 169-174.

Ahmad, M.S., Ashraf, M. and Hussain, M. (2011). Phytotoxic effects of nickel on yield and concentration of macro- and micro-nutrients in sunflower (*Helianthus annuus* L.) achenes. *J. Hazard Mater*. **185**(2-3), 1295-1303.

Ahmed, F., Hossain, M., Abdullah, A.T., Akbor, M. and Ahsan, M. (2016). Public health risk assessment of chromium intake from vegetable grown in the wastewater irrigated site in Bangladesh. *Pollution*. **2**: 425-432.

Ali, S., Bai, P., Zeng, F., Cai, S., Shamsi, I.H., Qiu, B., Wu, F. and Zhang, G. (2011). The ecotoxicological and interactive effects of chromium and aluminum on growth, oxidative damage and antioxidant enzymes on two barley genotypes differing in Al tolerance. *Environ. Exp. Bot.* **70**: 185-191.

Al-Saleh, I., Al-Rouqi, R., Elkhatib, R., Abduljabbar, M., Al-Rajudi, T. (2017). Risk assessment of environmental exposure to heavy metals in mothers and their respective infants. *Int. J. Hyg. Environ. Health*. **220**: 1252-1278.

Al-Weher, M. (2008). Levels of heavy metal Cd, Cu and Zn in three fish species collected from the Northern Jordan Valley. *Jordan J. Biol. Sci.* **1**: 41-46.

Anjum, S.A., Tanveer, M., Hussain, S., Shahzad, B., Ashraf, U., Fahad, S., Hussain, W., Jan, S., Khan, I., Saleem, M.F., Bajwa, A.A., Wang, L., Mahmood, A., Samad, R.A. and Tung, S.A. (2016a). Osmoregulation and antioxidant production in maize under combined cadmium and arsenic stress. *Environ. Sci. Pollut. Res*. https://doi.org/10. 1007/s11356-016-6382-1.

Anjum, S.A., Tanveer, M., Hussain, S., ullah, E., Wang, L., Khan, I., Samad, R.A., Tung, S.A., Anam, M. and Shahzad, B. (2016b). Morpho-physiological growth and yield responses of two contrasting maize cultivars to cadmium exposure. *Clean. Soil, Air, Water*. **44** (1): 29-36.

Anoduadi, C.O., Okenwa, L.B., Okieimen, F.E., Tyowua, A.T. and Uwumarongie-Ilori, E.G. (2009). "Metal immobilization in CCA contaminated soil using laterite and termite mound soil. Evaluation by chemical fractionation," *Nigerian J. Appl. Sci*. **27**: 77–87.

Arisseto-Bragotto, A.P. (2017). Food quality and safety progress in the Brazilian food and beverage industry: chemical hazards. *Food Qual. Saf*. **1**(2): 117-129.

Ashraf, A., Bibi, I., Niazi, N.K., Ok, Y.S., Murtaza, G., Shahid, M., Kunhikrishnan, A. and Mahmood, T. (2017). Chromium(VI) sorption efficiency of acid-activated banana peel over organo-montmorillonite in aqueous solutions. Int. J. Phytoremediat. microorganisms and bioremediation application potential: a review. *Int. Bio- deterior. Biodegr*. **59**: 8-15.

Atiemo, S., Ofuso, F., Mensah, K., Tutu, O., Palm, L. and Blackson, A. (2010). Contamination assessment of heavy metals in road dust from selected roads in Accra Ghana. *Res. J. Environ. Earth sci*. **3**: 473-480.

ATSDR (Agency for Toxic Substances and Disease Registry). (2004). Toxicological profile for cobalt. –gency for Toxic Substances and Disease Registry. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA.

ATSDR (Agency for Toxic Substances and Disease Registry). (2007). Toxicological Profile for Barium. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA.

Avudainayagam, S., Megharaj, M., Owens, G., Kookana, R.S., Chittleborough, D. and Naidu, R. (2003). Chemistry of Chromium in Soils with Emphasis on Tannery Waste Sites. Reviews of Environmental Contamination and Toxicology. *Springer*, pp. 53-91.

Babula, P., Adam, V., Opatrilova, R., Zehnalek, J., Havel, L. and Kizek, R. (2008). Uncommon heavy metals, metalloids and their plant toxicity: a review. *Environ. Chem. Lett*. 6, 189-213.

Baccouch, S., Chaoui, A. and Ferjani, E.E. (2001). Nickel toxicity induced oxidative damage in *Zea mays* roots. *J. Plant Nutr*. **24**(7): 1085-1097.

Bal, W. and Kasprzak, K.S. (2002). Induction of oxidative DNA damage by carcinogenic metals. *Toxicol. Lett. (Shannon)* **127**(1): 55-62.

Banks, M., Schwab, A. and Henderson, C. (2006). Leaching and reduction of chromium in soil as affected by soil organic content and plants. *Chemosphere*. **62**: 255-264.

Basu, N., Abare, M., Buchanan, S., Cryderman, D., Nam, D.H., Sirkin, S., Schmitt, S. and Hu, H. (2010). A combined ecological and epidemiologic investigation of metal exposures amongst Indigenous peoples near the Marlin Mine in Western Guatemala. Science of the Total Environment. **409**(1): 70-77.

Beckett, W.S., Nordberg, G.F. and Clarkson, T.W. (2007). Routes of exposure, dose and metabolism of metals, Seveir Amsterdam-Tokyo. 39-76.

Bellido-Milla, D.J.M., Moreno-Perez and Hernandez-Artiga, M.P. (2000). Differentiation and classification of beers with flame atomic spectrometry and molecular absorption spectrometry and sample preparation assisted by microwaves, Spectrochim. Acta, Part. 855-864.

Benderli-Cihan, Y., Sozen, S. and Oztürk-Yildirim, S. (2011). Trace elements and heavy metals in hair of stage III breast cancer patients. *Biol. Trace Element Res*. 144(1-3): 360-379.

Benlloch-González, M., Romera, J., Cristescu, S., Harren, F., Fournier, J.M. and Benlloch, M. (2010). K^+ starvation inhibits water-stress-induced stomatal closure via ethylene synthesis in sunflower plants. *J. Expt. Bot*. **61**(4): 1139-1145.

Bernard, A. (2008). Cadmium & its adverse effects on human health. *Indian J. Med. Res*. **128**(4):557–64.

Blanco, A. (2017). Accumulation of lead and associated metals (Cu and Zn) at different growth stages of soybean crops in lead-contaminated soils: food security and crop quality implications. *Environ. Earth Sci*. **76**: 182.

Borosova, D., Mocak, J., Beinrohr, E. and Miskovic, P. (2002). Validation and quality assurance of arsenic determination in urine by GFAAS after toluene extraction. *Polish J. Environ. Studies*. **11**: 617-623.

Broadway, A., Cave, M.R., Wragg, J., Fordyce, F.M., Bewley, R.J., Graham, M.C., Ngwenya, B.T. and Farmer, J.G. (2010). Determination of the bioaccessibility of chromium in Glasgow soil and the implications for human health risk assessment. *Sci. Total Environ*. **409**: 267—277.

Brochin, R., Leone, S., Phillips, D., Shepard, N., Zisa, D. and Angerio, A. (2008). The cellular effect of lead poisoning and its clinical picture. GUJHS. **5**(2): 1–8.

Brown, P.H. (2007). Nickel. In: Barker, A.V., Pilbean, D.J. (Eds.), Handbook of Plant Nutrition. CRC Taylor and Francis, New York, pp. 395-402.

Caldelas, C., Bort, J. and Febrero, A. (2012). Ultrastructure and subcellular distribution of Cr in Iris pseudacorus L. using TEM and X-ray microanalysis. *Cell Biol. Toxicol*. **28**: 57—68.

Castagnetto, J.M., Hennessy, S.W., Roberts, V.A., Getzoff, E.D., Tainer, J.A. and Pique, M.E. (2002). MDB: the metalloprotein database and browser at the Scripps Research Institute. *Nucleic Acids Res*. **30**(1):379–382.

CCME (Canada Council of Ministers of Environment). (2015). Canadian soil Quality Guidelines for the Protection of Environmental and Human Health. Canada Council of Ministers of the Environment Winnipeg.

Cempel, M. and Nikel, G. (2006). Nickel: a review of its sources and environmental toxicology. *Pol. J. Environ. Stud*. **15**(3): 375-382.

Chakraborty, S., Dutta, A.R., Sural, S., Gupta, D. and Sen, S. (2013). Ailing bones and failing kidneys: a case of chronic cadmium toxicity. *Ann. Clin. Biochem*. **50**(5): 492–495.

Challa, S. and Kumar, R. (2009). Nanostructured oxides.Weinheim, Germany: Wiley. P. 29.

Chan-Hon-Tong, A., Charles, M. A., Forhan, A., Heude, B. and Sirot, V. (2013). Exposure to food contaminants during pregnancy. *Sci. Total Environ*. **458-460**: 27- 35.

Chanpiwat, P. and Sthiannopkao, S. (2014). Status of metal levels and their potential sources of contamination in Southeast Asian rivers. *Environ. Sci. Pollut. Res*. **21**(1): 220-233.

Chatterjee, C. and Dube, B. K. (2005). Impact of pollutant elements on vegetables growing in sewage-sludge-treated soils. *J. Plant Nutr*. **28**(10): 1811-1820.

Chatterjee, J. and Chatterjee, C. (2003). Management of phytotoxicity of cobalt in tomato by chemical measures. *Plant Sci*. **164**(5): 793-801.

Chen-Huang, D. and Liu, J. (2009). Functions and toxicity of nickel in plants: recent advances and future prospects. *Clean. Soil, Air, Water*. **37**(4-5): 304-313.

Chrostowski, P., Durda, J.L. and Edelmann, K.G. (1991). The use of natural processes for the control of chromium migration. *Remediation,* **2**(3): 341–351.

Chukwuma, S.C. (1994). Evaluating baseline data for Lead (Pb) and Cadmium (Cd) in rice, yam, cassava and guinea grass from cultivated soils in Nigeria. *Toxicol. Environ. Chem*. **45**: 45-56.

Clarkson, T.W. (1988). Biological Monitoring of Toxic Metals; Plenum Press: New York, pp. 265-282.

Collins, R.N. and Kinsela, A.S. (2011). Pedogenic factors and measurements of the plant uptake of cobalt. *Plant Soil*. **339**(1): 499-512.

Cullaj, A., Hasko, A., McBow, I. and Kongoli, F. (2004). Investigation of the potential of several plants for phytoremediation of nickel-contaminated soils and for nickel phytoex*traction. Eur. J. Miner. Process. Environ. Protect*. **4**: 144-151.

Davila-Rangel, J.I. and Solache-Rios, M. (2006). Sorption of cobalt by two Mexican clinoptilolite rich tuffs zeolitic rocks and kaolinite. J. *Radioanalytical Nuclear Chem*. **270**(2): 465-471.

Delbari, S. and Kulkarni, D. (2011). Seasonal variations in heavy metal concentration in agricultural soils in Tehran, Iran. *Biosci. Discovery J*. **2**: 333-340.

Denkhaus, E. and Salnikow, K. (2002). Nickel essentiality, toxicity, and carcinogenicity. *Crit. Rev. Oncol.-Hematol*. **42** (1), 35-56.

Devi, G., Gopal-Bhattacharyya, K., Mahanta, L. B. and Devi, A. (2014). Trace metal composition of PM2.5, soil, and Machilus bombycina leaves and the effects on Antheraea assama silk worm rearing in the oil field area of northeastern India. *Water Air & Soil Pollut*. **225**: 1884-1897.

Dickin, S.K., Schuster-Wallace, C.J., Qadir, M., Pizzacalla, K. (2016). A review of health risks and pathways for exposure to wastewater use in agriculture. Environ. *Health Perspect*. **124**(7): 900-909.

D-Mello, J.P.G. (2003). Food Safety: Contaminants and toxins. CABI Publishing, Wallinford, Oxon, UK, Cambridge, MA, p. 480.

Dobrowolski, R. and Otto, M. (2012). Determination of nickel and cobalt in reference plant materials by carbon slurry sampling GFAAS technique after their simultaneous preconcentration onto modified activated carbon. *J. Food Composition Anal*. **26**(1-2): 58-65.

D-Oliveira, L.M., Ma, L.Q., Santos, J.A., Guilherme, L.R. and Lessl, J.T. (2014). Effects of arsenate, chromate, and sulfate on arsenic and chromium uptake and trans*location by arsenic hyperaccumulator Pteris vittata L. Environ. Pollut*. **184**: 187-192.

Dotaniya, M., Das, H. and Meena, V. (2014). Assessment of chromium efficacy on germination, root elongation, and coleoptile growth of wheat (Triticum aesti- vum L.) at different growth periods. En*viron. Monit. Assess*. **186**: 2957-2963.

D-Souza, F.B. and de-Lima Brandao, H., Hackbarth, F.V., de-Souza, A.A.U., Boaventura, R.A., de-Souza, S.M.G.U. and Vilar, V.J. (2016). Marine macro-alga Sargassum cymosum as electron donor for hexavalent chromium reduction to trivalent state in aqueous solutions. *Chem. Eng. J*. **283**: 903-910.

Economou-Eliopoulos, M., Megremi, I., Atsarou, C., Theodoratou, C. and Vasilatos, C. (2013). Spatial evolution of the chromium contamination in soils from the Assopos to Thiva Basin and C. Evia (Greece) and potential source (s): anthropogenic versus natural processes. *Geosciences*. **3**: 140-158.

Ediin, G., Golantu, E. and Brown, M. (2000). Essentials for health and wellness. Toronto, Canada: Bartlett Publishers. Pp. 368.

Edwards, A.C., Coull, M., Sinclair, A. H., Walker, R. L. and Watsun, C.A. (2012). Elemental status (Cu, Mo, Co, B, S and Zn) of Scottish agricultural soils compared with a soil-based risk assessment. *Soil Use & Management*. **28**(2): 167-176.

Elbagermi, M.A., Edwards, H.G.M. and Alajtal, A. I. (2014). Monitoring of HeavyMetal Content in Fruits and Vegetables Collected from Production andMarket Sites in theMisurata Area of Libya. *ISRN Anal. Chem*. pp. 1-5.

Eleftheriou, E.P., Adamakis, I.-D.S., Panteris, E. and Fatsiou, M. (2015). Chromium- induced ultrastructural changes and oxidative stress in roots of Arabidopsis thaliana. I*nt. J. Mol. Sci*. **16**: 15852-15871.

El-Hinnawi, E. and Hashmi, M.H. (1988). The State of Environment. United Nations Programme. Butterworths, London.

El-Kady, A.A., and Abdel-Wahhab, M.A. (2018). Occurrence of trace metals in foodstuffs and their health impact. *Trends Food Sci. Technol*. **75**: 36-45.

Environment Agency. (2009). Supplementary information for the derivation of SGV for nickel. Bristol: Environment Agency.

Ezigbo and Obiageli, V. (2015). Determination of heavy metals in fruit spices. *American J. Eng. Res. (AJER)*. **4**(12): 64-66.

FAO/WHO. (1999). Expert Committee on Food Additives, “Summary and conclusions,” in Proceedings of the 53rd Meeting Joint FAO/WHO Expert Committee on Food Additives, Rome, Italy, June 1999.

FAO/WHO. (2011). International Food Standards CODEX STAN-179. Codex Alimentarius commission, WHO/FAO, 2011.

Farooq, M., Ali, S., Hameed, A., Bharwana, S., Rizwan, M., Ishaque, W., Farid, M., Mahmood, K. and Iqbal, Z. (2016). Cadmium stress in cotton seedlings: physiological, photosynthesis and oxidative damages alleviated by glycinebetaine. *S. Afr. J. Bot*. **104**: 61-68.

Flora, S.J.S., Mittal, M. and Mehta, A. (2012). Heavy metal induced oxidative stress & its possible reversal by chelation therapy. *Indian J. Med. Res*. **128**: 501–523.

Flyvholm, M.A., Nielsen, G.D. and Andersen, A. (1984). Nickel content of food and estimation of dietary intake. Z. Lebensm. Unters. *Forsch*. **179**(6): 427-431.

Foster, W. G., Cheung, A. P., Davis, K., Graves, G., Jarrell, J., Leblanc, A., Liang, C. L., Leech, T., Walker, M., Weber, J.P. and Von-Oostdam, J. (2012). Circulating metals and persistent organic pollutant concentrations in Canadian and non-Canadian born primiparous women from five Canadian centres: results of a pilot biomonitoring study. *Science of the Total Environment*. **435-436**: 326-336

Gall, J.E., Boyd, R.S. and Rajakaruna, N. (2015). Transfer of heavy metals through terrestrial food webs: a review. *Environ. Monit. Assess*. **187**: 201.

Gerhardsson, L., Dahlin, L., Knebel, R. and Schutz A. (2002). Blood lead concentration after a shotgun accident. *Environ Health Perspect*. 1**1**0(1):115–117.

Ghani A. (2011). Effect of chromium toxicity on growth, chlorophyll and some mineral nutrients of *Brassica juncea* L. *Egyptian Acad J. Biol Sci.* **2**(1): 9-15.

Ghosh, R., Xalxo, R., Gope, M.C., Mishra, S., Kumari, B. and Ghosh, M. (2011). Estimation of heavy metals in locally available vegetables collected from roadside market sites (1-4) of different area of Ranchi city. *Pharmbit*. **23&24**(1&2): 68-73.

Gill, R.A., Ali, B., Islam, F., Farooq, M.A., Gill, M.B., Mwamba, T.M. and Zhou, W. (2015). Physiological and molecular analyses of black and yellow seeded Brassica napus regulated by 5-aminolivulinic acid under chromium stress. *Plant Physiol*. *Biochem*. **94**: 130-143.

Gomez, K. A. and Gomez, A. A. (1984). Statistical Procedure for Agricultural Research (2nd edn.). *Intl. Rice Res*. *Inst. A Willey Int. Sci*., pp. 188-192.

Gopal, R., Dube, B. K., Sinha, P. and Chatterjee, C. (2003). Cobalt toxicity effects on growth and metabolism of tomato. *Communications in Soil Sci. Plant Anal*. 34(5-6): 619-628.

Goyer, R.A. (1990). Lead toxicity: from overt to subclinical to subtle health effects. *Environ Health Perspect*. **86**:177–181.

Gregson, S. and Hope, A. (1994). Review of Phytotoxicity, Uptake and Accumulation of Elements and Organic Chemicals in Terrestrial Higher Plants, AERC Report for Department of the Environment, London.

Gress, J., de Oliveira, L.M., da Silva, E.B., Lessl, J.M., Wilson, P.C., Townsend, T. and Ma, L.Q. (2015). Cleaning-induced arsenic mobilization and chromium oxidation from CCA-wood deck: potential risk to children. *Environ. Int*. **82**: 35-40.

Han, J.X., Shang, Q. and Du, Y. (2009). Effect of environmental cadmium pollution on human health. *Health*. **1**(3):159–166.

Hedfi, A., Mahmoudi, E., Boufahja, F., Beyrem, H. and Aissa, P. (2007). Effects of increasing levels of nickel contamination on structure of offshore nematode communities in experimental microcosms. *Bull. Environ. Contam. Toxicol*. **79**(3): 345-349.

Henson, M.C. and Chedrese, P.J. (2004). Endocrine disruption by cadmium, a common environmental toxicant with paradoxical effects on reproduction. *Exp. Biol. Med (Maywood)*. **229**(5):383–392.

Hoque, M. E. (2003). Arsenic and other heavy metal status in soils and vegetables in Chapai Nawabganj. MS Thesis, Department of Soil Science, BangladeshAgricultural University, Mymensingh, Bangladesh.

Hostynek, J.J., Dreher, F., Nakada, T., Schwindt, D., Angbogu, A. and Mailbach, H.I. (2001). Human stratum corneum adsorption of nickel salts. Investigation of depth profiles by tape stripping in vivo. Acta DermatoVenereological, Supplement. **212**: 11-18.

Hsu, L.C., Liu, Y.T. and Tzou, Y.M. (2015). Comparison of the spectroscopic speciation and chemical fractionation of chromium in contaminated paddy soils. *J. Hazard. Mater*. 296: 230-238.

Hu, J., Wu, F., Wu, S., Cao, Z., Lin, X. and Wong, M.H. (2013). Bioaccessibility, dietary exposure and human risk assessment of heavy metals from market vegetables in Hong Kong revealed with an in vitro gastrointestinal model. *Chemosphere*. **91**: 455-461.

Hussain, M.B., Ali, S., Azam, A., Hina, S., Farooq, M.A., Ali, B., Bharwana, S.A. and Gill, M.B. (2013). Morphological, physiological and biochemical responses of plants to nickel stress: a review. *Afr. J. Agric. Res*. **8**: 1596-1602.

IARC (International Agency for Research on Cancer). (1987). Overall Evaluations of Carcinogenicity: an Updating of IARC Monographs Volumes 1 to 42. World Health Organization, International Agency for Research on Cancer.

IARC (International Agency for Research on Cancer). (1993). Cadmium and cadmium compounds. In Beryllum, Cadmium, Mercury and exposure in Glass manufacturing Industry. IARC Monographs on the evaluation of carcinogenic risks to humans, International Agengy for Research on Cancer, Lyon. **58**:119-237.

Ijeoma, L., Ogbonna, P. and Ogbonna, C. (2011). Heavy Metal content in soil and Medicinal plants in high traffic urban area. **10**: 618-624

Irfan, M., Hayat, S., Ahmad, A. and Alyemeni, M.N. (2013). Soil cadmium enrichment: Allocation and plant physiological manifestations. *Saudi J Biol Sci*. **20**(1):1-10.

Islam, M.K., Khanam, S., Lee, S.Y., Alam, I. and Huhl, M.R. (2014). The interaction of arsenic (As) and chromium (Cr) influences growth and antioxidant status in tossa jute (*Corchorus olitorius*). *Plant Omics*. **7**: 499.

Jahan, S., Gosh, T., Begum, M. and Saha, B.K. (2011). Nutritional profile of some tropical fruits in Bangladesh: Specially anti-oxidant vitamins and minerals. *Bangladesh J. Medical Sci*. **10** (2): 95-103.

Jaison, S. and Muthukumar, T. (2016). Chromium accumulation in medicinal plants growing naturally on tannery contaminated and non-contaminated soils. *Biol. Trace Elem. Res*. 1-13.

Jamali, M.K., Kazi, T.G. and Arian, M.B. (2007). Determination of Pollution Indices. *Environmental Pollution Handbook, China*. Pp. 209-218.

Jamil, M., Zeb, S., Anees, M., Roohi, A., Ahmad, I., Rehman, S. and Rha, E.S. (2014). Role of *Bacillus licheni formis* in phytoremediation of Nickel contaminated soil cultivated with rice. *Int. J. Phytoremediation*. **16**: 554-571.

Jaradat, M. and Momani, A. (1999). Contamination of roadside soil, plants and air with heavy metals in Jordan, a comparison study. *Turk J. Chem.* **23**: 209-220.

Jarup, L. (2003). Hazards of heavy metals contamination. Br. *Med. Bull*. **68**:167-182.

Jayasiri, H. B., Vennila, A. and Purushothaman, C.S. (2014). Spatial and temporal variability of metals in inter-tidal beach sediment of Mumbai, India. *Environ. Monitor. Assess*. **186**(2): 1101-1111.

Jonnalagadda, S.B., Kindeness, A., Kubayi, S. and Cele, M.N. (2008). Macro, minor and toxic elemental uptake and distribution in Hypoxis hemerocallidea, “the African Potato”- an edible medicinal plant. *J. Environ. Sci. Health*. **43**(3): 271- 280.

Kabata-Pendias, A. (2010). Trace Elements in Soils and Plants. CRC press.

Kabata-Pendias, A. and Mukherjee, A.B. (2007). Trace elements from Soil to Human. Berlin: Springer- Verlag.

Kabata-Pendias, A. and Pendias, H. (1992). Trace elements in soils and plants. CRC Press, London.

Kabata-Pendias, A. and Pendias, H. (2001). Trace elements in Soils and Plants. 3rd Edn. Boca Raton: CRC Press, London.

Kamran, M.A., Eqani, S.A.M.A.S., Katsoyiannis, A., Xu, R.-K., Bibi, S., Benizri, E. and Chaudhary, H.J. (2016). Phytoextraction of chromium (Cr) and influence of Pseudomonas putida on Eruca sativa growth. *J. Geochem. Explor*. http:// dx.doi.org/10.1016/j.gexplo.2016.09.005.

Kaplan, O., Yildirim, N. and Tayhan, N. (2011). Assesment of some heavy metals in drinking water of Tunceli. Turkey. *E-J. Chem*. **8**: 276-280.

Khalid, S., Shahid, M., Niazi, N.K., Murtaza, B., Bibi, I., Dumat, C. (2017). A comparison of technologies for remediation of heavy metal contaminated soils. *J. Geochem. Explor*. **182** (B): 247-268.

Khan, S., Rehman, S., Khan, A.Z., Khan, M.A. and Shah, M.T. (2010). Soil and vegetables enrichment with heavy metals from geological sources in Gilgit, northern Pakistan. *Ecotoxicol. Environ. Saf*. **73**: 1820-1827.

Kisamo, H. (2003). Environmental hazards associated with heavy metals in Lake Victoria Basin (East Africa). *African Newsletter on Occupational Health and Safe*ty; **13**: 67-69.

Koch, D., Nies, D.H. and Grass, G. (2007). The RcnRA (YohLM) system of Escherichia coli: a contection between nickel, cobalt and iron homeostasis. *Biometals*. **20**(5): 759-771.

Kosiorek, M. and Wyszkowski, M. (2019a). Content of macronutrients in oat (Avena sativa L.) after remediation of soil polluted with cobalt. *Environ. Monitor. Assess*. **191**(389): 1-15.

Kosiorek, M. and Wyszkowski, M. (2019b). Effect of neutralising substances on reducing influence of cobalt on the content of selected elements in soil. *Int. Agrophysics*. **33**(2): 153-159.

Kosiorek, M. and Wyszkowski, M. (2019c). Effect of neutralizing substances on the content of trace elements in soil contaminated with cobalt. Environment *Protection Eng*. **45**(1): 45-55.

Kranner, I. and Colville, L., (2011). Metals and seeds: biochemical and molecular implications and their significance for seed germination. E*nviron. Exp. Bot*. **72**: 93-105.

Kumar, A. and Seema. (2016). Accumulation of Heavy Metals in Soil and Green Leafy Vegetables, Irrigated with Wastewater. *J. Environ Sci Toxic Food Tech*. **10**(10): 8-19.

Kumar, P., Mandal, B. and Dwivedi, P. (2013). Phytoremediation for defending Heavy Metal Stress in Weed Flora. *Int. J. Agric. Environ. Biotechnology*. **6**(4): 647-656.

Kumari, V., Yadav, A., Haq, I., Kumar, S., Bharagava, R.N., Singh, S.K. and Raj, A. (2016). Genotoxicity evaluation of tannery effluent treated with newly isolated hex- *avalent chromium reducing Bacillus cereus. J. Environ. Manage*. **183**: 204-211.

Lake, D.L., Kirk, P.W.W. and Lester, J.N. (1984). The fractionation, characterization and speciation of heavy metals in sewage sludge and sewage sludge amended soils: Areview. *J. Enviro. Qual*. **13**: 175-183.

Lalah, J.O., Njogu, S.N. and Wandiga, S.O. (2009). The effects of Mn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+} and Zn^{2+} ions on pecticide adsorption and mobility in a topical soil. *Bulletin of Environmental Contamination & Toxicology*. **83**(3): 352-358.

Lente, I., Keraita, B., Dreshsell, P., Ofosu, J., Abdul, A. and Brimah, K. (2013). Risk assessment of heavy metal contamination on vegetables grown in long term wastewater irrigated urban farming sites in Accra, Ghana. *Water Quality, Exposure and Health*. **4**(4): 179-186.

Li, X.L., Chen, C.L., Chang, P.P., Yu, S. M., Wu, W.S. and Wang, X.K. (2009). Comparative studies of cobalt sorption and desorption on bentonite, alumina and silica: effect of pH and fulvic acid. *Desalination*. **244**(1-3): 283-292.

Lilli, M.A., Moraetis, D., Nikolaidis, N.P., Karatzas, G.P. and Kalogerakis, N. (2015). Characterization and mobility of geogenic chromium in soils and river bed sediments of Asopos basin. *J. Hazard. Mater*. **281**: 12-19.

Liu, J., Duan, C.Q., Zhang, X.H., Zhu, Y.N. and Hu, C. (2009). Subcellular distribution of chromium in accumulating plant Leersia hexandra Swartz. Plant Soil. **322**: 187-195.

Lock, K., De Schamphelaere, K. A. C., Because, S., Criel, P., Van Eeckhout, H. and Janssen, C.R. (2006): Development and validation of an acute biotic ligand model (BLM) predicting cobalt toxicity in soil to the potworm Enchytraeus albidus. *Soil Biol. Biochem*. **38**(7): 1924-1932.

Ma, H.W., Hung, M.L. and Chen, P.C. (2007). A systemic health risk assessment for the chromium cycle in Taiwan. E*nviron. Int.* **33**: 206—218.

Machlin, L.J. and Bendich, A. (1987). Free radical tissue damage: protective role of antioxidant nutrients. *J. Federation American Soc. Expt. Biol*. **1**: 441-445.

Mahdavian, E. and Somashekar, R.K. (2009). Heavy metals and safety of fresh fruits in Bangalore city, India - A case study. *J. Sci. Eng. Technol*. **1**(5): 17-27.

Maleki, and Zarasvand, M.A. (2008). Heavy metals in selected edible vegetables and estimation of their daily intak in Sananday, Iran. *South East Asian J. Tropical. Med. Public Health*. **39**:335-340.

Mamtaz, R. and Chowdhury, H. (2006). Leaching characteristics of solid waste at an urban solid waste dumping site. *J. Civil Eng.* **34**: 71-79.

Markowitz, M. (2000). Lead Poisoning. *Pediatr Rev*. **21**(10):327–335.

Marshall, F., Agarwal, E., Lintelo, D., Bhupal, D.S., Singh, R.P.B., Mukherjee, N. and Sen, C. (2003). Heavy Metals Contamination of Vegetables in Delhi. Technical Report of UK Department for International Development. 48-51.

Martin, S. and Griswold, W. (2009). Human health effects of heavy metals. Environmental Science and Technology Briefs for Citizens. **15**: 1–6.

Mathew, B.B., Tiwari, A. and Jatawa, S.K. (2011). Free radicals and antioxidants: A review. *J. Pharma. Res*. **4**(12):4340–4343.

Mebrahtu, G. and Zebrabruk, S. (2011). Concentration of heavy metals in drinking water from urban areas of the Tigray Region, Northern Ethiopia. *Maejo Int. J. Sci. Technol.* **3**: 105-121.

Mico, C., Peris, M., Sanchez. and Recatala, L. (2006). Heavy metal content of agricultural soils in a Mediterranean Semiarid area: the Segura River Valley (Alicante, Spain). *Spanish J. Agric. Res.* **4**: 363-372.

Mishra, D. and Kar, M. (1974). Nickel in plant growth and metabolism. *Bot. Rev*. **40**: 395-452.

Mohanty, M. and Patra, H.K. (2011). Attenuation of chromium toxicity by bioremediation technology. R*ev. Environ. Contam. Toxicol*. **210**: 1-34.

Mohiuddin, K.M., Otomo, K., Ogawa, Y. and Shikazono, N. (2012): Seasonal and spatial distribution of trace elements in the water and sediments of the Tsurumi River in Japan. *Environ. Monitor. Assess*. **184**(1): 265-279.

Molas, J. (1998). Changes in morphological and anatomical structure of cabbage (*Brassica oleracea* ***L***.) outer leaves and in ultrastructure of their chloroplasts caused by an in vitro excess of nickel. *Photosynthetica (Prague)*. **34**(4): 513-522.

Monudu, M. and Anyakora, C. (2010). Heavy metal contamination of ground water. *The Serulere Case Study J*. **2**:39-40.

Moody, R.P., Joncas, J., Richardson, M., Petrovic, S. and Chu, I. (2009). Contaminated Soils (II): In vitro dermal absorption of nickel (Ni – 63) and mercury (Hg – 203) in human skin. *J. Toxicol. Environ. Health, Part A*. **72**: 551-559.

Mostafa, M., Azrina, A., Mohd-Yunus, A.S., Mohd-Zakiuddin, S., Mohd-Izuan-Effendi, H. and Muhammad-Rizal, R. (2012). Heavy metals (mercury, arsenic, cadmium, plumbum) in selected marine fish and shellfish along the Straits of Malacca. *Int Food Res J*. **19**(1):135–140.

Mudgal, V., Madaan, N., Mudgal, A., Singh, R.B. and Mishra, S. (2010). Effect of toxic metals on human health. *Open Nutraceuticals J*. **3**:94–99.

Mustafiz, A., Ghosh, A., Tripathi, A.K., Kaur, C., Ganguly, A.K. and Bhavesh, N.S. (2014). A unique Ni^{2+} dependent and methylglyoxal-inducible rice glyoxalase I possesses a single active site and functions in abiotic stress response. *Plant J*. **78**: 951-963.

Mutlu, A., Lee, B.K., Park, G.H., Yu, B.G. and Lee, C.H. (2012). Long-term concentrations of airborne cadmium in metropolitan cities in Korea and potential health risks. *Atmos Environ*. **47**:164–173.

Mwegoha, W. and Kihampa, C. (2010). Heavy metal contamination in agricultural soils and water in Dares Salaam City, Tanzania. *African J. Environ. Sci. Technol*. **4**: 763-769.

Najeeb, U., Ahmad, W., Zia, M.H., Malik, Z. and Zhou, W. (2014). Enhancing the lead phytostabilization in wetland plant *Juncus effusus* L. through somaclonal manipulation and EDTA enrichment. *Arab J Chem*.

Nandi, S., Srivastava, R.C. and Agarwal, K.M. (2012). Accumulation of heavy metals by Solanum melonuma irrigated with wastewater. *Int. J. Agric. Environ. Biotechnol*. **5**(4): 329- 332.

Narendrula, R., Nkongolo, K. K. and Beckett, P. (2012). Comparative soil metal analyses in Sudbury (Ontario, Canada) and Lubumbashi (Katanga, DR-Kongo). *Bulletin of Environmental Contamination & Toxicology*. **88**(2): 187-192.

Nielsen, F.H. (1980). Interaction of Nickel with essential minerals. pp. 611-634 in J O Nriagu (Ed). Nickel in the Environment. John Wiley & Sons, New York.

Nirmal-Kumar, J.I., Soni, H. and Kumar, R.N. (2007). Characterization of heavy metals in vegetables using inductive coupled plasma analyzer (ICPA). *J. Environ. Sci. Manag*. **11**(3): 75-79.

Nriagu, J.O. (1988). Production and Uses of Chromium. Chromium in the Natural and Human Environments. Wiley, New York, pp. 81-104.

Obiri, S. (2007). Determination of heavy metals in water from boreholes in Dumasi in the Wassa West District of western region of Republic of Ghana. *Environ. Monitor. Assess*. **130**(1-3): 455-463.

Ochieng, E. Z., Lalah, J. O. and Wandiga, S. O. (2008). Water quality and trace metal distribution in a pristine Lake in the Lake basin in Kenya. *Bulletin of Environmental Contamination & Toxicology*. **80**(4): 362-368.

Oh, Y.J., Song, H., Shin, W.S., Choi, S.J. and Kim, Y.H. (2007). Effect of amorphous silica and silica sand on removal of chromium (VI) by zero-valent iron. *Chemosphere*. **66**: 858-865.

Pandey, G. and Madhuri, S. (2010). Significance of Fruits and Vegetables in Malnutrition Cancer. *Plant Arch*. **10**(2): 517-22.

Pandey, N. and Sharma, C.P. (2002). Effect of heavy metals Co^{2+}, Ni^{2+} and Cd^{2+} on growth and metabolism of cabbage. *Plant Sci*. **163**(4): 753-758.

Papadopoulos, A., Prochaska, C., Papadopoulos, F., Gantidis, N. and Metaxa, E. (2007). Determination and evaluation of cadmium, copper, nickel, and zinc in agricultural soils of Western Macedonia, Greece. *Environ. Manag*. **40**(4): 719-726.

Papanikolaou, N.C., Hatzidaki, E.G., Belivanis, S., Tzanakakis, G.N. and Tsatsakis, A.M. (2005). Lead toxicity update. A brief review. *Med Sci Monitor*. **11**(10): 325-329.

Patrick, L. (2003). Toxic metals and antioxidants: Part II. The role of antioxidants in arsenic and cadmium toxicity. *Altern Med Rev*. **8**(2):106–128.

Pereira, Y., Lagniel, G., Godat, E., Baudouin-Cornu, P., Junot, C. and Labarre, J. (2008). Chromate causes sulfur starvation in yeast. T*oxicol. Sci*. **106**: 400-412.

Pietrodangelo, A., Pareti, S. and Perrino, C. (2014). Improved identification of transition metals in airborne aerosols by SEM-EDX combined backscattered and secondary electron microanalysis. *Environ. Sci. Pollut. Res*. **21**(6): 4023-4031.

Pitot, C.H. and Dragan, P.Y. (1996). Chemical carcinogenesis, 5th edition: In Casarett D. (ed), Toxicology Inter. Edi., McGraw Hill, Newyork. 210-260.

Pourbaix, M. (1974). Atlas of Electrochemical Equilibria, Pergamon Press, New York, NY, USA, Translated from French by J.A. Franklin.

Pourrut, B., Shahid, M., Dumat, C., Winterton, P. and Pinelli, E. (2011). Lead uptake, *toxicity, and detoxification in plants. Rev. Environ. Contam. Toxicol*. **213**: 113-136.

Prado, F.E., Hilal, M., Chocobar-Ponce, S., Pagano, E., Rosa, M. and Prado, C. (2016). Chapter 6-Chromium and the Plant: a Dangerous Affair. Aahmad, Parvaiz. Plant Metal Interaction. *Elsevier*, pp. 149-177.

Prakash, D., Upadhyay, G., Gupta, C., Pushpangadan, P. and Singh, K.K. (2012). Antioxidant and free radical scavenging activities of some promising wild edible fruits. *Int. Food Res. J*. **19**(3): 1109-1116.

Qingjie, G., Jun, D., Yunchuan, X., Qingfei, W. and Liqiang, Y. (2008). Calculating Pollution Indices by Heavy Metals in Ecological Geochemistry Assessment and a Case Study in Parks of Beijing. *J. China Univ. Geosci*. **19**(3): 230-241.

Quantin, C., Ettler, V., Garnier, J. and Sebek, O. (2008). Sources and extractibility of chromium and nickel in soil profiles developed on Czech serpentinites. Co*mptes Rendus Geosci*. **340**: 872—882.

Radwan, M. A. and Salama, A.K. (2006). Market basket survey for some heavy metals in Egyptian fruits and vegetables. *Food Chem. Toxicol.* **44**(8): 1273-1278.

Rahman, H., Sabreen, S., Alam, S. and Kawai, S. (2005). Effects of nickel on growth and composition of metal micronutrients in barley plants grown in nutrient solution. *J. Plant Nutr*. **28**(3): 393-404.

Rai, P.K. (2018). Phytoremediation of Emerging Contaminants in Wetlands. CRC Press, Taylor & Francis, Boca Raton, Florida, USA, pp. 248.

Rancelis, V., Cesniene, T., Kleizaite, V., Zvingila, D. and Balciuniene, L. (2012). Influence of cobalt uptake by Vicia faba seeds on chlorophyll morphosis induction, SOD polymorphism, and DNA methylation. *Environ. Toxicol*. **27**(1): 32-41.

Reale, L., Ferranti, F., Mantilacci, S., Corboli, M., Aversa, S., Landucci, F., Baldisserotto, C., Ferroni, L., Pancaldi, S. and Venanzoni, R. (2016). Cyto-histological and morpho-physiological responses of common duckweed (Lemna minor L.) to chromium. *Chemosphere*. **145**: 98-105.

Rodriguez, J.H. (2014). Assessment of Pb and Zn contents in agricultural soils and soybean crops near to a former battery recycling plant in Cordoba, Argentina. *J. Geochem. Explor*. **145**: 129-134.

Rognerud, S., Dauvalter, V. A., Fjeld, E., Skjelkvale, B. L., Christensen, G. and Kashulin, N. (2013). Spatial trends of trace-element contamination in recently deposited lake sediment around the Ni-Cu smelter at nikel, Kola Peninsula, Russian Arctic. *AMBIO*. **42**(6): 724- 736.

Roychowdhury, T., Tokunaga, H. and Ando, M. (2003). Survey of arsenic and other heavy metals in food composites and drinking water and estimation in dietary intake by the villages from an arsenic-affected area of West Bengal, India. *Sci. Total Environ*. **308**:15-35.

Ryuko, S., Ma, Y., Ma, N., Sakaue, M. and Kuno, T. (2012). Genome-wide screen reveals novel mechanisms for regulating cobalt uptake and detoxification in fission yeast. *Molecular Genetics and Genomics*. **287**(8): 651-662.

Saad, R., Kobaissi, A., Robin, C., Echevarria, G. and Benizri, E. (2016). Nitrogen fixation and growth of Lens culinaris as affected by nickel availability: a pre-requisite for optimization of agromining. *Environ. Exp. Bot*. **131**: 1-9.

Sajib, M.A.M., Hoque, M. M., Yeasmin, S. and Khatun, M.H.A. (2014). Minerals and heavy metals concentration in selected tropical fruits of Bangladesh. *Int. Food Res. J*. **21**(5): 1731-1736.

Salt, D.E., Kato, N., Kramer, U., Smith, R.D. and Raskin, I. (2000). The role of root exudates in nickel hyperaccumulation and tolerance in accumulator and nonaccumulator species of Thlaspi. In: Terry, N., Banuelos, G. (Eds.), Phytoremediation of Contaminated Soil and Water. CRS Press LLC, London, pp. 189-200.

Santos, C. and Rodriguez, E. (2012). Review on Some Emerging Endpoints of Chromium (VI) and Lead Phytotoxicity. INTECH Open Access Publisher.

Satarug, S., Garrett, S.H., Sens, M.A. and Sens, D.A. (2011). Cadmium, environmental exposure, and health outcomes. Ciência & Saúde Coletiva. **16**(5): 2587–2602.

Sathawara, N.G., Parikish, D.J. and Agrwal, Y.K. (2004). Essentials heavy metals in environmental samples from western Indian. Bull. *Environ. Cont. Toxicol*. **73**: 756-761.

Scott, D., Keoghan, J.M. and Allen, B.E. (1996). Native and low input grasses-A New Zealand high country perspective. *New Zealend J Agric. Res*. **39**: 499-512.

Scragg, A. (2006). Environmental Biotechnology, Oxford University Press, Oxford, UK, 2nd edition.

Selinus, O. and Alloway, B. (2005). Essentials of medical geology: impact of the natural environment. London, UK: Blackie Academic and Professional Publishers. Pp 187.

Seregin, I.V. and Kozhevnikova, A.D. (2006). Physiological role of nickel and its toxic effects on higher plants. *Russ. J. Plant Physiol*. **53**(2): 257-277.

Shahid, M., Khalid, S., Abbas, G., Shahid, N., Nadeem, M., Sabir, M., Aslam, M. and Dumat, C. (2015). Heavy metal stress and crop productivity. In:

Hakeem, K.R. (Ed.), Crop Production and Global Environmental Issues SE - 1. Springer International Publishing, pp. 1-25.

Shahid, M., Pourrut, B., Dumat, C., Nadeem, M., Aslam, M. and Pinelli, E. (2014). Heavy metal induced reactive oxygen species: phytotoxicity and physicochemical changes in plants. R*ev. Environ. Contam. Toxicol*. 1-44.

Shahzad, B., Mughal, M.N., Tanveer, M., Gupta, D. and Abbas, G. (2017). Is lithium biologically an important or toxic element to living organisms? *Environ. Sci. Pollut. Res*. **24**: 103-115.

Shahzad, B., Tanveer, M., Zhao, C., Rehman, A., Cheema, S.A., Shams ur, Rehman, Sharma, A., Song, H. and Zhaorong, D. (2018). Role of 24-epibrassinolide (EBL) in mediating heavy metal and pesticide induced oxidative stress in plants. *Ecotoxicol. Environ. Saf*. **147**: 935-944.

Shanker, A.K., Cervantes, C., Loza-Tavera, H. and Avudainayagam, S. (2005). Chromium toxicity in plants. *Environ. Int*. **31**: 739-753.

Sharma, A., Song, H. and Zhaorong, D. (2018). Role of 24-epibrassinolide (EBL) in mediating heavy metal and pesticide induced oxidative stress in plants. *Ecotoxicol. Environ. Saf*. **147**: 935-944.

Sharma, P. and Dubey, R.S. (2005). Lead toxicity in plants. *Brazilian J. Plant Physiol*. **17**(1):35–52.

Sharma, R.K., Agarwal, M. and Marshall, F.M. (2008a). Atmospheric deposition of heavy metals (Cu, Zn, Cd and Pd) in Varanasi City, India. *Environ. Monit. Assess*. **142**:269-278.

Sharma, R.K., Agarwal, M. and Marshall, F.M. (2008b). Heavy metal (Cu, Zn, Cd and Pd) contamination of vegatables in urban India: A Case study in Varanasi. *Environ. Pollut*. **154**:254-263.

Sheppard, P.R., Speakman, R.J., Ridenour, G., Glascock, M. D., Farris, C. and Witten, M.L. (2007). Spatial patterns of tungsten and cobalt in surface dust of Fallon, Nevada. *Environ. Geochem. Health*. **29**(5): 405-412.

Shi, G. and Cai, Q. (2009). Leaf plasticity in peanut **(***Arachis hypogea* L.) in response to heavy metal stress. En*viron. Exp. Bot*. **67**: 112-117.

Shukla, O., Dubey, S. and Rai, U. (2007). Preferential accumulation of cadmium and chromium: toxicity in Bacopa monnieri L. under mixed metal treatments. Bull. En*viron. Contam. Toxicol*. **78**: 252—257.

Simeonov, L., Kolhubovski, M. and Simeonov, B. (2010). Environmental heavmetal pollution and effects on child mental development. Dordrecht, Netherlands: Springer. Pp 114-115.

Singh, A., Sharma, R.K., Agrawal, M. and Marshall, F.M. (2010). Risk Assessment of Heavy Metal Toxicity through Contaminated Vegetables from Waste Water Irrigated Area of Varanasi, *India. Int. Soci. Trop. Eco*. **51**: 375-87.

Singh, V. and Chandel, S. (2006). Analytical study of heavy metals of industrial Effluents at Jaipur, Rajasthan (India). *J. Environ. Sci***.** *Eng*. **48**: 103-108.

Sinha, S., Saxena, R. and Singh, S. (2005). Chromium induced lipid peroxidation in the plants of Pistia stratiotes L.: role of antioxidants and antioxidant enzymes. *Chemosphere*. **58**, 595-604.

Smith, L.A., Means, J.L. and Chen, A. (1995). Remedial Options for Metals-Contaminated Sites, Lewis Publishers, Boca Raton, Fla, USA.

Sobukola, O.P., Adeniran, O.M., Odedairo, A.A. and Kajihausa, O.E. (2010). "Heavy metal levels of some fruits and leafy vegetables from selected markets in Lagos, Nigeria." *African J. Food Sci*. **4**(2): 389-393.

Solomons, N.W., Viteri, F., Shuler, T.R. and Nielsen, F.H. (1982). Bioavailability of nickel in man: Effects of foods and chemically defined dietary constituents on the absorption of inorganic nickel. *J. Nutr*. **112**(1): 39- 50.

Soylak, M., Cihan, Z. and Yilmaz, E. (2012). Evaluation of trace element contents of some herbal plants and spices retailed in Kayseri, Turkey. *Environ. Monitor. Assessm*. **184**(6): 3455-3461.

Sreekanth, T.V.M., Nagajyothi, P.C., Lee, K.D. and Prasad, T.N.V.K.V. (2013). Occurrence, physiological responses and toxicity of nickel in plants. *Int. J. Environ. Sci. Technol*. **10**(5): 1129-1140.

Swarnalatha, K., Letha, J. and Ayoob, S. (2013). An investigation into the heavy metal burden of Akkulam-Veli Lake in south India. *Environ. Earth Sci*. **68**(3): 795- 806.

Tappero, R., Peltier, E., Grafe, M., Heidel, K., Ginder-Vogel, M., Livi, K.J.T., Rivers, M.L., Marcus, M.A., Chaney, R.L. and Sparks, D.L. (2007). Hyperaccumulator Alyssum murale relies on a different metal storage mechanism for cobalt than for nickel. *New Phytologist*. **175**(4): 641-654.

Teo, J., Goh, K., Ahuja, A., Ng, H. and Poon, W. (1997). Intracranial vascular calcifications, glioblastoma multiforme, and lead poisoning. *AJNR*. **18**: 576-579.

Thakali, S., Allen, H.E., Di Toro, D.M., Ponizovsky, A.A., Rooney, C.P., Zhao, F.J. and McGrath, S.P. (2006). A terrestrial biotic ligand model. 1. Development and application to Cu and Ni toxicity to barley root elongation in soils. E*nviron. Sci. Technol*. **40**: 7085-7093.

Thompson, H.C. and Kelly, W.C. (1990). Vegetable Crops. 5th Edn., McGraw Hill Publishing Company Ltd., New Delhi.

Thurmer, K., Williams, E. and Reutt-Robey, J. (2002). Autocatalytic oxidation of lead crystallite surfaces. *Science*. **297**(5589):2033–2035.

Thyssen, J.P., Jensen, P., Liden, C., Julander, A., Jellesen, M.S., Menne, T. and Johansen, J.D. (2011). Assessment of nickel and cobalt release from 200 unused hand-held work tools for sale in Denmark-Sources of occupational metal contact dermatitis. *Science of the Total Environ*. **409**(22): 4663-4666.

Tiwari, K., Dwivedi, S., Singh, N., Rai, U. and Tripathi, R. (2009). Chromium (VI) Induced Phytotoxicity and Oxidative Stress in Pea (*Pisum Sativum* L.): Biochemical Changes and Translocation of Essential Nutrients.

Trejo-Tapia, G., Jimenez-Aparicio, A., Rodriguesz-Monroy, M., De Jesus-Sanchez, A. and Gutierrez-Lopez, G. (2001). Influence of cobalt and other microelements on the production of betalains and the growth of suspension cultures of Beta vulgaris. *Plant Cell Tissue & Organ Culture*. **67**(1): 19-23.

Trichopoulos, D. (1997). Epidemiology of cancer. In: DeVita, V.T. (Ed.), Cancer: Principles and Practice of Oncology. Lippincott Company, Philadelphia, pp. 231-258.

Turkhall, R.M., Skowronski, G.A., Abdel-Rahman, M.S. (2008). Effects of soil and aging on the dermal bioavailability of hydrocarbons and metals in soil. *Int. J. Soil Sediment Water*. **1**(1): 1-13

Uddin, I., Bano, A. and Masood, S. (2015). Chromium toxicity tolerance of Solanum nigrum L. and Parthenium hysterophorus L. plants with reference to ion *pattern, antioxidation activity and root exudation. Ecotoxicol. Environ. Saf*. **113**: 271—278.

Ulusoy, H.I., Gurkan, R., Demir, O. and Ulusoy, S. (2012). Micelle-mediated extraction and flame atomic absorption spectrometric method for determination of trace cobalt ions in beverage samples. *Food Analytical Methods*. **5**(3): 454-463.

Underwood, E.J. (1977). Trace Elements in Human and Animal Nutrition, fourth ed., Academic Press, New York.

UN-HABITAT (United Nations Human Settlement Programme). (2004). The State of the World's Cities: Globalization and Urban Culture. UN-HABITAT, Human Settlements Programme, Nairobi.

Upadhyaya, D., Survaiya, M.D., Basha, S., Mandal, S.K., Thorat, R.B., Haldar, S., Goel, S., Dave, H., Baxi, K., Trivedi, R.H. and Mody, K.H. (2014). Occurrence and distribution of selected heavy metals and boron in groundwater of the Gulf of Khambhat region, Gujarat, India. *Environ. Sci. Poll. Res*. **21**(5): 3880-3890.

USEPA (US Environmental Protection Agency). (1986). Health assessment document for nickel and nickel compounds. EPA Report 600/8-83/012FF, p. 460.

Usero, J., Morillo, J. and Gracia, I. (1997). Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*. **55**(3): 431-44

Verma, A., Sharma, P., Dhusia, N. and More, N. (2016). Determination of heavy metal content in fruits and fruits juices consume in urban areas of Lucknow, India. *Int. J. Food Sci. Nutr*. **1**(5): 44-50.

Wadhwa, N., Mathew, B.B., Jatawa, S. and Tiwari, A. (2012). Lipid peroxidation: mechanism, models and significance. *Int. J. Curr. Sci.* **3**:29–38.

WHO. (1992). Cadmium, Environmenatl Health Criteria, Geneva. 134.

WHO. (1995). Lead. Environmental Health Criteria, Geneva. 165.

WHO. (2003). Evaluation of certain food additives and contaminants (Thirty-third report of the joint FAO/WHO expert report series No. 790, WHO, Geneva.

Wieczorek, J., Wieczorek, T. and Bieniaszewski, T. (2004). Cd and lead content in cereal grains and soil from cropland adjacent to roadways. *Polish J. Agric. Studies.* **14**: 535-540.

Wogu, D. and Okaka, E. (2011). Pollution studies on Nigerian rivers: Heavy metals in surface water of warri River, Delta state. *J. Biodiver. Environ. Sci*. **1**: 7-12.

Wong, C.S.C., Li, X.D., Zhang, G., Qi, S.H. and Peng, X.Z. (2003). Atmospheric depositions of heavy metals in the Pearl River Delta, China. *Atmos. Environ*. **37**:767-776.

Wo-Niak, K. and Basiak, J. (2003). Free radicals-mediated induction of oxidized DNA-bases and DNA protein cross-links by nickel chloride. *Mutat. Res. Genet. Toxicol. Environ. Mutagen*. **514**: 233-243.

Wyszkowski, M. and Wyszkowska, J. (2007). The content of macroelements in spring barley (Hordeum vulgare L.) and thiers relations with the enzymatic activity of cobalt contaminated soil. Proceeding of SECOTOX Conference and the International Conference on Environmental Management, Engineering, Planning and Economics. **1**: 181-186.

Wyszkowski, M. and Wyszkowska, J. (2009). The effect of contamination with cadmium on spring barley (Hordeum vulgare L.) and its relationship with the enzymatic activity of soil. *Fresenius Environmental Bulletin*. **18**(7): 1046-1053.

Xiong, T., Austruy, A., Pierart, A. and Shahid, M. (2016a). Kinetic study of phytotoxicity induced by foliar lead uptake for vegetables exposed to fine particles and implications for sustainable urban agriculture. *J. Environ. Sci*. 1-12.

Xiong, T., Dumat, C., Pierart, A., Shahid, M., Kang, Y., Li, N., Bertoni, G. and Laplanche, C. (2016b). Measurement of metal bioaccessibility in vegetables to improve human exposure assessments: field study of soil-plant-atmosphere transfers in urban areas, South China. *Environ*. *Geochem*. *Health*. **38**(6): 1283-1301.

Yadav, S.K., Dhote, M., Kumar, P., Sharma, J., Chakrabarti, T. and Juwarkar, A.A. (2010). Differential antioxidative enzyme responses of Jatropha curcas L. to chromium stress. *J. Hazard. Mater*. **180:** 609—615.

Yongsheng, W., Qihui, L. and Qian, T. (2011). Effect of Pb on growth, accumulation and quality component of tea plant. *Procedia Eng*. **18**:214–219.

Zaidi, M.I., Asrar, A., Mansoor, A. and Farooqui, M.A. (2005). The heavy metal concentrations along roadsides trees of Quetta and its effects on public health. *J Appl. Sci*. **5**(4):708-711

Zamani-Hargalani, F., Karbassi, A., Monavari, S. M. and Abroomand Azar, P. (2014). A novel pollution index based on the bioavailability of elements: a study on Anzali wetland bed sediments. – *Env. Monitor. Assessm*. **186**(4): 2329-2348.

Zayed, A.M. and Terry, N. (2003). Chromium in the environment: factors affecting biological remediation. *Plant Soil*. **249**: 139-156.

Zhou, H. (2016). Accumulation of heavy metals in vegetable species planted in contaminated soils and the health risk assessment. *Int. J. Environ. Res. Public Health*. **13**(3): 289.

APPENDICES

Appendix I. Mean square of heavy metal concentration in collected fruit samples from Shwapno super shop of Mirpur 10 in Dhaka city

Sources of variation	Degrees of freedom	Mean square				
		Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)
Replication	2	0.012	0.001	0.001	0.001	0.001
Factor A	4	0.021*	0.011	0.004	0.003	0.002
Error	8	NS	NS	NS	NS	NS

Appendix II. Mean square of heavy metal concentration in collected fruit samples from Agora super market of Dhanmondi in Dhaka city

Sources of variation	Degrees of freedom	Mean square				
		Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)
Replication	2	0.001	0.001	0.001	0.001	0.001
Factor A	4	0.014**	0.006	0.005	0.004	0.003
Error	8	0.003	NS	NS	NS	NS

Appendix III. Mean square of heavy metal concentration in collected fruit samples from Prince Bazar of Mirpur-1 in Dhaka city

Sources of variation	Degrees of freedom	Mean square				
		Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)
Replication	2	0.002	0.0011	0.001	0.001	0.001
Factor A	4	0.008**	0.007	0.004	0.006	0.002
Error	8	0.002	NS	NS	NS	NS

NS = Non-significant * = Significant at 5% level ** = Significant at 1% level

Appendix IV. Mean square of heavy metal concentration in collected fruit samples from Kawran Bazar fruit market of Kawran Bazar in Dhaka city

Sources of variation	Degrees of freedom	Mean square				
		Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)
Replication	2	0.002	0.003	0.001	0.001	0.001
Factor A	4	0.018**	0.008	0.004	0.012	0.003
Error	8	0.003	NS	NS	NS	NS

NS = Non-significant * = Significant at 5% level ** = Significant at 1% level

Appendix V. Mean square of heavy metal concentration in collected fruit samples from Meena Bazar of Shyamoli in Dhaka city

Sources of variation	Degrees of freedom	Mean square				
		Lead (Pb)	Cadmium (Cd)	Chromium (Cr)	Nickel (Ni)	Cobalt (Co)
Replication	2	0.003	0.002	0.001	0.001	0.001
Factor A	4	0.012**	0.008	0.004	0.003	0.002
Error	8	0.001	NS	NS	NS	NS

NS = Non-significant * = Significant at 5% level ** = Significant at 1% level

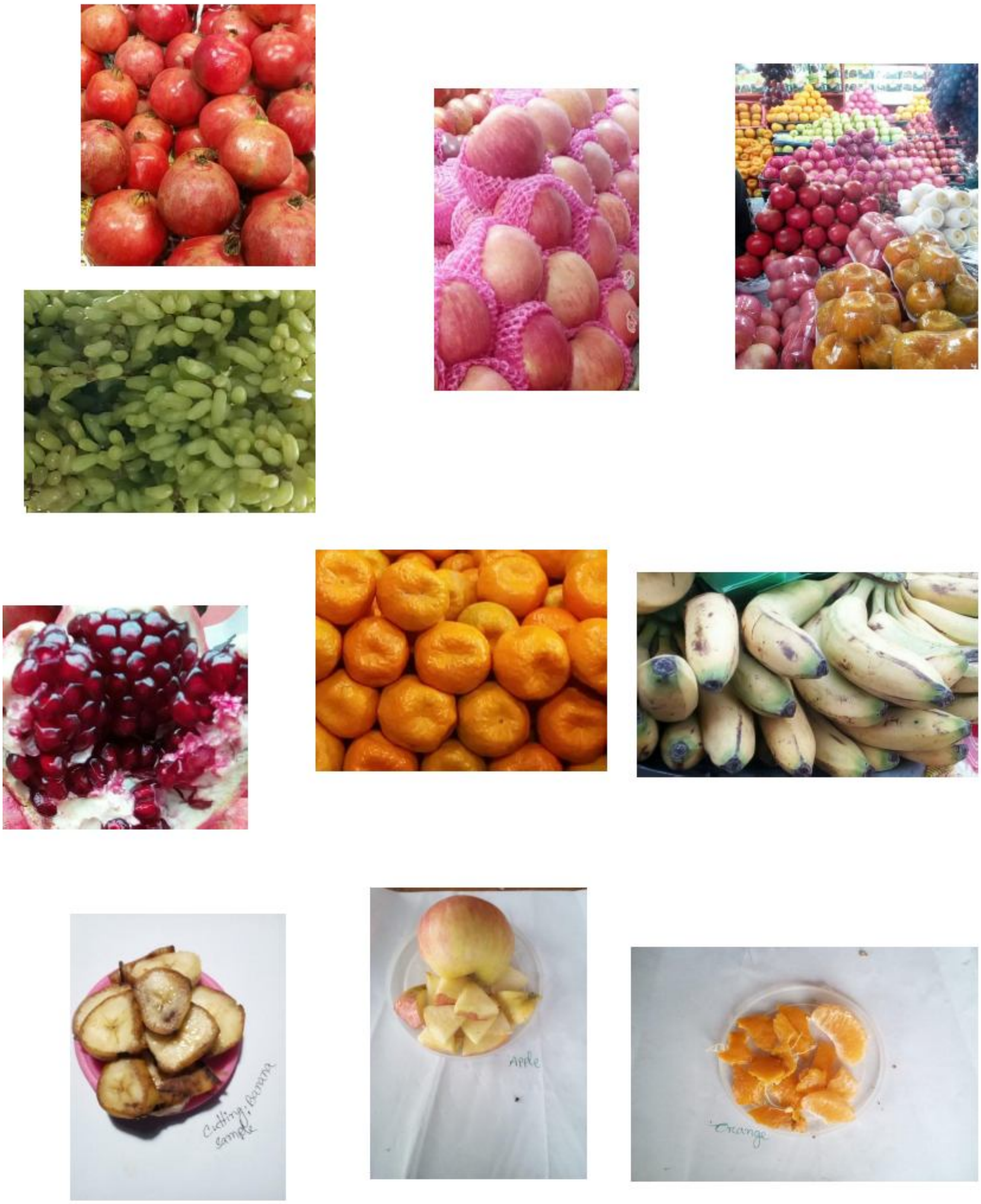

Plate 1. Photographs showing sample collection and cutting