DETERMINATION OF HEAVY METALS FROM PESTICIDE

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CERTIFICATE

This is to certify that the thesis entitled **"DETERMINATION OF HEAVY METALS FROM PESTICIDE"** 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 bona fide research work carried out by **MST. JAKIA FERDOUSI**, Registration No. **20-11083** 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, 2022

Dhaka, Bangladesh

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Dedicated To

My Beloved Parents

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ABSTRACT

This study was carried out at the laboratory of Agricultural Chemistry Department, Sher-e-Bangla Agricultural University, Sher-e-Bangla Nagar, Dhaka, from the month of June 2022 to April 2023 for the determination and risk analysis of heavy metals in different pesticide samples collected from different places in Bangladesh. Three places namely (1) Monirampur, Jessore, (2) Barinagar, Jessore, (3) Mithapukur, Rangpur was selected for sample collection. Samples were collected on four groups namely (i) Carbamate, (ii) Imidachloprid (iii) Organophosphate and (iv)Pyrithroid. Total thirty eight samples were considered for the present study. Atomic absorption spectroscopy analysis was used to determine lead (Pb), chromium (Cr) and cadmium (Cd) in sample pesticides. It was found that the levels of heavy metals in pesticides varied from group to group. Some concentrations of Pb, Cr, and Cd in pesticide samples some were higher and some were lower than the acceptable limit recommended by FAO/WHO. According to FAO/WHO, the maximum allowable concentration for Pb, Cr and Cd are 0.3, 2.3 and 0.2 mg/L respectively. Among 38 samples 12 samples were contaminated with lead (Pb) concentrations and these were belonged to organophosphate group. Single factor pollution index (PI) indicates that some of pesticide samples are contaminated (PI>1) and some are yet not contaminated (PI<1). In case of sum of pollution index (SPI), sample Dursban of organophosphate group showed the highest SPI (2.58) whereas the lowest SPI (0.32) was found in Jubas of pyrithroid group. Again considering metal pollution index (MPI), the highest MPI (0.250) was at sample pesticide Starban of organophosphate group whereas the lowest MPI (0.028) was at sample pesticide Genethrin of pyrithroid group. Government should monitor the imported pesticide to reduce the contamination with heavy metals with different methods of heavy metal detections. Presence of heavy metal in pesticide regarding Pb, Cr and Cd is harmful if it is higher than acceptable limit recommended by FAO/WHO.

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ABBREVIATIONS AND ACRONYMS

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)
ml = MiliLitre
M.S. = Master of Science
No. = Number
SAU = Sher-e-Bangla Agricultural University
% = Percentage
NaOH = Sodium Hydroxide
mg = Miligram
P = Phosphorus
ppm = Parts Per Million
K = Potassium
Ca = Calcium
L = Litre
Mg = Microgram
USA = United States of America
WHO = World Health Organization

CHAPTER ONE

INTRODUCTION

Heavy metals are metals that have a relatively high density, atomic weight or atomic number. A heavy metal can be defined on the basis of density, where individual criteria in physics may be the atomic number, while a chemist may be more concerned with chemical behavior. Metals with a high atomic number and density greater than 5 gm/cm^3 are known as heavy metals (Zhang *et al.,* 2019). The main constituents of heavy metals are chromium (Cr), manganese (Mn), cobalt (Co), copper (Cu), zinc (Zn), molybdenum (Mo), mercury (Hg), nickel (Ni), tin (Sn), lead (Pb), cadmium (Cd), antimony (Sb) etc. Some heavy metals are known as essential nutrients (such as iron, cobalt and zinc) while others are relatively harmless (such as ruthenium, silver and indium). But these can be toxic in large quantities or certain forms. Some heavy metals such as lead, cadmium and mercury are highly toxic.

The sources of heavy metal pollution are natural processes and anthropogenic activates. Soil may inherit heavy metals from the original material which are obtained from metal rich rocks including serpentine and black shale (He *et al.,* 2005). Anthropogenic sources of heavy metal pollution include odor, mining, waste disposal, fossil fuel combustion, erosion and agricultural practices. The first major human influence on the soil was agriculture (Scragg, 2006).By using fertilizers for growth and completion of the life cycle plants need not only macronutrients (N, P, K, S, Mg, and Ca) but also essential micronutrients, which are sources of heavy metals. Some soils may have heavy metal deficiencies (such as Cu, Co, Mn, Fe, Ni, Mo and Zn) which are essential for the healthy growth of plants (Lasat, 2000). Another source of heavy metal is pesticide. Pesticide helps to control herbs, pests and insects which are harmful for the agricultural production. The use of municipal and industrial wastewater in agriculture is also responsible for heavy metal pollution. Studies in several cities in Asia and Africa have shown that agriculture based on wastewater irrigation is responsible for 50% of vegetable supply in urban areas (Bjuhr, 2007).

The risk of heavy metals pollution in the environment is increasing rapidly and is having a detrimental effect, especially in the agriculture through soil accumulation and plant adoption (Toth *et al.,* 2016).The problem of heavy metals pollution has become more complex. Although some heavy metals are required for various organs of both plants and humans, they become toxic when their concentration exceeds the certain level (according to FAO/WHO the maximum allowable limits for Pb, Cr and Cd is 0.3, 2.3 and 0.2 respectively). Agriculture and industry influence heavy metal pollution greatly, affects agricultural soils and vegetation especially in industrial areas (Xiao *et al.,* 2017).Heavy metal deposits can be described as a deposit of ecosystem elements. An important point of contact of plants for heavy metal ions transmitted from the soil. They have a tendency to stabilize and attach contaminants to the soil, thus reducing their bioavailability. These metals can harm plants and harm human health through infections in the food chain (Cho-Ruk *et al.,* 2006, Tanghau *et al.,* 2011). Soil is a basic provision of food grain and can be greatly affected by heavy metals from point sources and non-point sources. Advantageous soil insects (especially in agriculture), invertebrates, small and large mammals are all affected (Gall et al., 2015; Bartrons and Penuelas, 2017; Rai *et al.,* 2018).Many medicinal plants have been exposed to organic deposits of various metals (e.g., Cd, As, Cr, Cd, Cu, Pb, and Fe) while growing near industrial areas (Hamiani *et al.*, 2015; Bolan et al., 2017; Kim *et al.*, 2017a, 2017b; Kohzadi *et al.,* 2018). Greenhouse vegetables are also heavily contaminated with heavy metals such as Cu, Zn, Mn, Pb, and Cd (but not Fe) compared to open field vegetables, probably due to their low precision (Li *et al.,* 2017a, 2017b).

Heavy metals are not necessary for plant growth they are absorbed and deposited by plants at high levels which cause toxic damage to cells and tissues as a result of complex interaction of major toxic ions with other necessary or unnecessary ions (Ahmadpour, *et al.*, 2012). When these toxic heavy metals and trace elements contaminate soil and water, the plant system absorbs and stores these toxic elements. Prolonged consumption of these contaminated vegetables by humans can lead to major harmful diseases as a result of biodegradation. Lead (Pb) causes adverse problems in various organs and tissues including blood, central nervous system, kidneys and reproductive and immune systems of all animals and adversely affects the brainpower of children (Jamal *et al.,* 2018). Cadmium (Cd) is mainly stored in the human kidneys and liver, causing serious problems in these organs (Chen *et al.,* 2014). Short-term Cd intake is toxic, even in low concentrations and it is considered as a potential carcinogen. Excessive Cd exposure can cause lung problems such as alveolitis, bronchiolitis and emphysema (Aluko *et al.,* 2018; Qasemi *et al.,* 2019). High concentrations of Zn can affect growth and reproduction and cause health problems, such as flatulence, skin irritation, vomiting, nausea and anemia (Larake*b et al.,* 2017).

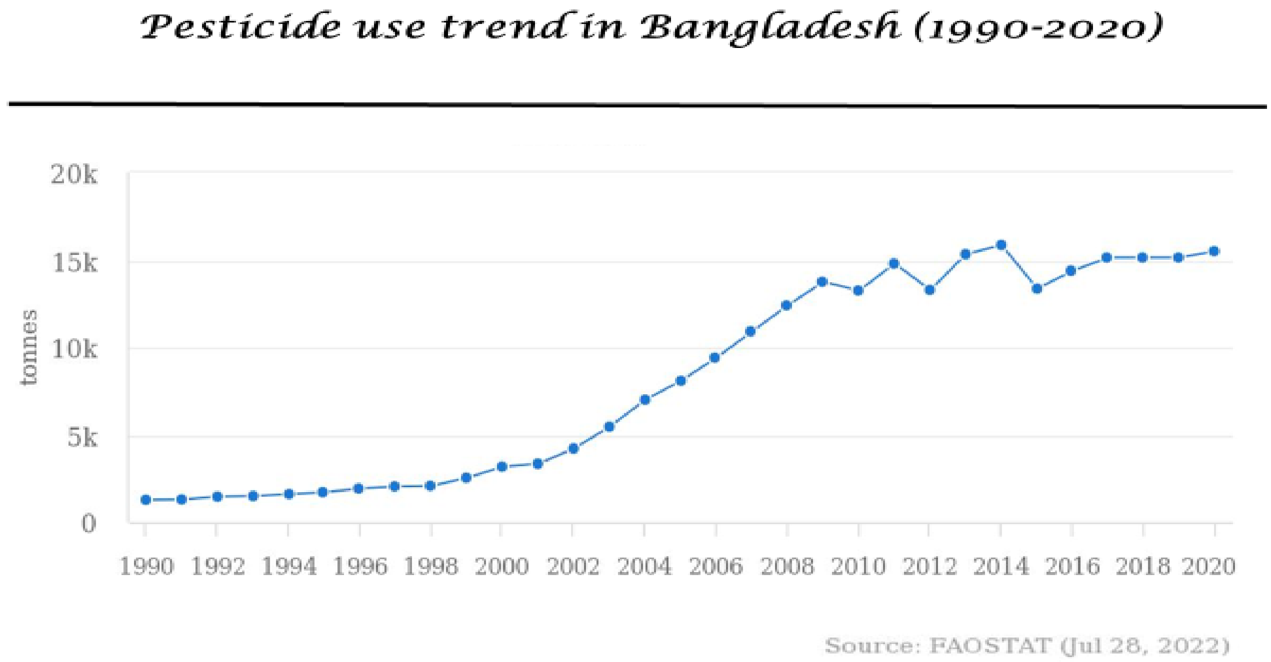
High concentrations of copper can cause severe mucosal irritation and erosion, extensive capillary problems, hepatic and renal problems, irritation and depression of the central nervous system (Celebi *et al.,* 2016).Exposure to Cr induces dermatitis, allergic skin damage and gastrointestinal ulcers (Sharma and Weng, 2007; Hazrati *et al.,* 2016). However, when it enters the human body for long periods of time, even small quantities of this substance can have harmful effects to humans.

About 10% of the chemicals have been approved for use in the recent past, as pesticides and fungicides in the UK are based on compounds containing Cu, Hg, Mn, Pb, or Zn. Examples of such pesticides are copper fungicide sprays such as Bordeaux mixture (copper sulphate) and copper oxychloride (Jones and Jarvis, 1981).To control some parasitic insect Lead arsenate has been used in fruit orchards for many years. Cu, Cr and as containing compounds were also widely used to control cattle ticks and to control pests in banana in New Zealand and Australia, where the soil concentration of these elements are much higher than the background density. This type of contamination is likely to cause problems, especially if the sites are rebuilt for other agricultural or non-agricultural purposes. Compared with fertilizers, the use of such materials has become more localized, limited to specific sites or crops (Lombi and Gerzabek, 1998).

The overall history of the use of synthetic pesticide in crop production is less than 150 years and the use boost up actually after the invention of DDT in 1939.

In Bangladesh, pesticides (insecticides) were not used till 1956. In that year Govt. imported only 3MT of pesticides to control pests. Up to 1974, the Govt. promoted the use of pesticides by supplying the cost to farmers (providing 100% subsidy). 1974-1979 with 50% subsidy and from 1979 the Govt. withdrew the subsidy completely and the business was handed over to the private sector. Current in total 33 thousand MT formulated product consume yearly.

Comparing with other pesticides fungicide is used larger amount in quantity and this also in the month of January to March (Bangladesh Crop Protection Association, 1216).



Source: FAOSTAT (Jul 28, 2022)

Figure 1.1 Status of pesticide use in Bangladesh (1990-2020)

There is not enough information whether these pesticides are also a considerable reason of metal pollution in Bangladesh context. Therefore, this study is aimed at determining the concentration of heavy metals (Pb, Cd, Cr) from pesticides. Bangladesh Food Safety Authority (BFSA) also found some contaminated samples with Pb, Cr and Cd.

Keeping all the problems related to heavy metal contamination the present research work was conducted with the following objectives-

The overall objective of the research is to determine the heavy metals (Pb, Cr, Cd) in pesticide.

1. To determine the level of heavy metal in pesticides available in a selective local market.
2. To assess the health risk of the heavy metal by the applied pesticides.

CHAPTER TWO

REVIEW OF LITERATURE

2.1 Definition of heavy metals

There are different types of definitions for heavy metals have been proposed. Some are based on density, some on atomic number or atomic weight and some on toxicity or chemical properties. The term heavy metals has been called "misinterpretation" in an IUPAC technical report due to the contradictory definitions and its lack of a "coherent scientific basis" (Duffus, 2002). Heavy metals occur individually or within the compounds (Martin and Griswold, 2009) and have effect on ecological quality on which they are exposed (Sastre *et al.,* 2002). Most common known pollutant heavy metals are Lead, Cadmium, Chromium, Copper, Arsenic, Mercury, Nickel and Zinc (Marais, 2009; Khayatzadeh and abbasi, 2010; Opaluwa *et al.,* 2012).

2.2 Source of heavy metal in agricultural soils

The main sources of heavy metals to the environment are direct contamination from mining and industrial processes and waste from mining activities, industrial and domestic processes (Madyiwa, 2006). Inputs of heavy metals to agricultural soils can occur from a variety of sources. These include land application of biosolids, fertilizers, pesticides, livestock manure, agrochemicals, irrigation water to the land and from atmospheric deposition. Some of the concerns about accumulation of heavy metals in agricultural soils stem uptake (Grubinger from their possible negative impacts on soil fertility and in some case their potential to accumulate in the human chain (McLaugh *et al.,* 1999; Gray *et al.,* 2003). Some metals like cadmium and lead are good indicators of contamination in soils because they appear in gasoline, car components, lubricants, industrial and incinerator emissions (Alloway, 1990; Li *et al.,* 2007).

2.3 Characteristics of heavy metals

Organic contaminants undergo microbial or chemical degradation, heavy metals have features which make them persistent and accumulate in the environment (Marques *et al.,* 2009). Elevated levels of heavy metals in soil increase plant uptake (Mkumbo, 2012). When plants are eaten by animals and humans, accumulation of metals along the food chain occurs. Humans can therefore build up high levels of the substances (Martin and Griswold, 2009). Since health effects connected to heavy metals are usually shown after a long time of exposure, the metals can biomagnified unnoticed in an ecosystem until they reach toxic levels (Marques *et al.,* 2009). Metals bind to the ground through adsorption mechanisms to different colloid particles in the soil. These particles are especially humus, hydrous oxides and allumino-silicate clays. The adsorption varies with pH, since a large amount particle surface has an electrical charge which is changeable cations, there among ions from heavy metals, bind more strongly at high pH. Cu, Pb and Zn are adsorbed for pH-levels above 4.5. The precipitation of Cr varies as it can from two redox formations, one being a cation and the other an anion (Gustafssn, 2008). High organic matter in soils indicate that there are a large amount of particle surfaces to which metals can be adsorbed and hence be less available for plant (Ross, 2011).

2.4 Mechanisms of heavy metals

Neal and Guilarte (2012) reported that the heavy metal ions from complexes with proteins, in which carboxylic acid ($-COOH$), amine ($-NH_2$), and Thiol ($-SH$) groups are involved. These modified biological molecules lose their ability to function properly and result in the malfunction or death of the cells. When metals bind to these groups, they inactive important enzyme systems, or affect protein structure, which is linked to the catalytic properties of enzymes. This type of toxin may also cause the formation of radicals, dangerous chemicals that cause the oxidation of biological molecules.

2.5 Heavy metals in fertilizer

Most of the chemical fertilizers are known to contain a different level of heavy metals originated from raw materials which remain with impurities during the fertilizers manufacturing processes (USEPA, 1999; MDH, 2008). Several studies show that fertilizers produced from rock phosphates are among the fertilizers with the high level of contaminations (Ukpabi *et al.,* 2012). Another study shows that the use of fertilizers in agricultural activities will increase the chromium metal content in crops, as the fertilizer is manufactured from phosphate ore will have the high content of heavy metals such as chromium, lead and iron (Saadie and Nabila, 2013). Also the study conducted by Ukpabi *et al.* (2012) in Nigeria shows that elements Mo, Mg, Fe, Ni, Zn, Cd, Mn, Cu, Co,Pb, Cr and B were reported on the three NPK fertilizers (15:15:15, 20:10:10 and 27:13:13) marketed in Nigeria, in this study Mo was observed to be above maximum acceptable concentration of 20 mg/kg in all the samples. Hence results from human health risk assessments are available for application of arsenic, cadmium, lead mercury and nickel found in fertilizers applied to agricultural soils (Salem *et al.,* 2002). According to CDFA, 2004, human health and the environment arising from the use of fertilizers could contain excessive criticism to the fertilizer industries, mainly because the involvement of these industries in operations that endanger the environment, where the main factor is the use of raw materials containing toxic metals such as cadmium (Cd), lead (Pb) and chromium (Cr) in the manufacture of fertilizers (Goncalves *et al.,* 2011).

The study of Affonso *et al.* (2014), shows the presence of toxic metals in fertilizers has been reported in the major food producing countries, like the United States, China and Brazil. According to reports developed by the United States Environment Protection Agency (USEPA, 2002) and the Weinberg Group (2001) (requested by The Fertilizer Institute), the main contaminants that are found in agricultural fertilizers are Cd, Cr, Co, Cu, Pb, Mo, Ni, Zn, arsenic (As), mercury (Hg), selenium (Se) and vanadium (V). Another case reported in the literature is the contaminants in raw materials from China. In a publication from the Washington Department of Ecology (WDE, 2000), it was reported in the presence of Cd in raw materials for the manufacture of fertilizers, with samples showing more than 20% of Cd, i.e., more than 200,000 ppm. It is also reported that the final products produced with the use of these contaminated sources presented 10,600 ppm of Cd. The presence of harmful elements in fertilizers is worrying because until the 70’s, most fertilizers were obtained directly from ores found in nature, and although they also contained toxic metals (Goncalves *et al.,* 2000). Overuse of fertilizers can also provide soil contamination it increases the concentration of a particular element or substance of environmental interest above its naturally occurring in the soil (Manzatto *et al.,* 2002). The study conducted by Hall Robarge (2004) found that some products contain high levels of heavy metal contaminants such as lead, arsenic, or cadmium.

2.6 Heavy metals in pesticides

Jamil *et al.* (2011) reported a high level of heavy metals Pb, Cd, Cr, Zn and Fe in two pesticide samples (Fenthion and Carbaryl) studied in Kedah and Penang, Malaysia. Gracia *et al.* (1996) evaluated heavy metals contents in two herbicides and one fungicide, in their analysis, all three pesticides were reported to contain similar content of Cd, however the two herbicides were found to have as the well high concentration of Fe, Mn, Zn, Pb and Ni. Application of chemical pesticides is also mentioned to be among important source of heavy metals in soil (Yin *et al.*, 2012). Although the use of some pesticides has been prohibited for containing harmful metals such as Cd, Hg and Pb, there are other products containing elements such as Zn and Cu which are still in use (Luo *et al.*, 2010). Shorett *et al.* (2010), found that pesticides pose both human health and the environment. The World Health Organization (WHO) also found that one million people suffered from pesticides and related health issues 20,000 of which resulted in death (WHO, 2002).

The concentration of Cd, Pb and Cu in leaves, stem and roots of maroon Spinach treated with pesticides are higher than the untreated Spinach (Chiroma *et al.*, 2007).

In Bangladesh, over 80% of pesticides are used in rice fields and the rapid increase of pesticide use is causing a detrimental effect on environment and health of farm workers and consumers (Parveen and Nakagoshi, 2001; Mourato and Huxley, 2000). The excessive application of pesticides in Indonesia during the 1970s and 1980s in agricultural activities caused serious environmental problems, such as acute and chronic human pesticide poisoning, animal poisoning, and the contamination of agricultural products (Yasmin and Souza, 2010).

2.7 Composition and Concentration of Heavy Metals in Soil

Several Studies which determine concentrations of heavy metals in paddy soils have been conducted in several places in the world (Atafar *et al.*, 2010, Jamil *et al.*, 2011, Yin *et al.*, 2012, Ghaderi *et al.*, 2012). Common of these studies was carried out in farms which apply fertilizers and pesticides. The outcomes of the studies show that there is a variation of concentrations of heavy metals in soils with the type of application of fertilizers and pesticides. Uses of inorganic products such as phosphate and micronutrient fertilizers were found to be the main contributor of soil heavy metals compared to organic products (MDH, 2008). The most up to date studies conducted in many countries, where rice is cultivated in a large amount, have declared high concentration values of heavy metals in soil (Jamil *et al.*, 2011, Atafar *et al.*, 2010). For examples the studies conducted by Atafar *et al.* (2010) and Ghaderi *et al.* (2012) in Iran, reported the high concentration of arsenic that was more than two times higher than Canadian standards. Cu and Cr were found to be approximately doubled in concentration in soil samples treated with fertilizers in comparison with controlled soil samples. Furthermore, Atafar *et al.* (2010) pointed out that high level of heavy metals in soil was contributed by the application of zinc sulfate fertilizers in the studied area. In another study in Malaysia, Khairiah *et al.* (2009) and Jamil *et al.* (2011) reported in common high levels of Mn, Fe, Zn, Cu, Cr, Pb and, Cd in paddy soil analyzed at Ketara, Besut, Terengganu, Kedah, Penang and Perlis. Fe and Mn were measured at higher concentrations than the rest of the heavy metals. Furthermore, the study related the concentration of Fe, Mn and Cd to the long term and repeated use of chemical fertilizers and pesticides in the cultivation areas. In Tanzania, composition and concentration of soil heavy metals in rice farms as a result of the application of chemical fertilizers and pesticides have been reported (Semu and Singh, 1995; Little and Lee, 2009).

The study conducted by Little and Lee (2009) shows high concentration values of soil metals Mg, P, Ca, Ti and Mn in farms receiving high fertilizer content and copper fungicides in Iringa district. Machiwa (2010) reported heavy metals concentrations of paddy soil in four sites (Geita, Mwanza city, Magu and Bunda) of Lake Victoria Basin where Cd, Pb and Hg were measured although in low concentrations. The study of Najat and Rashid (2015) also reported high concentrations of heavy metals at Cheju rice farms in Zanzibar.

2.8 Accumulation and distribution of heavy metals in paddy plants

The following studies shows how heavy metals accumulated and distributed in paddy plants, the study conducted at the East Coast of India by Deepmala *et al.* (2014) shows that those heavy metals get accumulated in different parts of paddy plant (Oryza sativa L.) including the grains, Mn and Cd are found to be accumulated more in shoot than in root and the ranking order of distribution for heavy metals was Zn > Mn > Cd > Cu > Cr > Pb. Another study of Linxian *et al.* (2013), conducted at China indicate that metals concentrations in root are always the highest one among all the plant organs and in the spike is the lowest and also found that compared with Flooding Irrigation (FI) rice, Non-Flooding controlled Irrigation (NFI) resulted in higher metal concentrations, of Cd, Cu and Pb. Also in Malaysia the study of Yap *et al.* (2009), found that Fe was the most predominant metal ion in the rice grains and roots, while Mn was the most predominant metal in the rice husks leaves and shoots.

Heavy metals in the environment are a health hazard due to their persistence of bioaccumulation and toxicity to plants, animals and human beings (Sharma and Dubey, 2005). The heavy metal accumulated in different parts of plants followed the sequence: root > stem > leaf (Ahmet *et al.*, 2005). Also it has been reported that crop plants have different abilities to absorb and accumulate heavy metals in their body parts and that there is a broad difference in metal uptake and translocation between plant species and even between cultivars of the same plant species (Kurz, 1999).

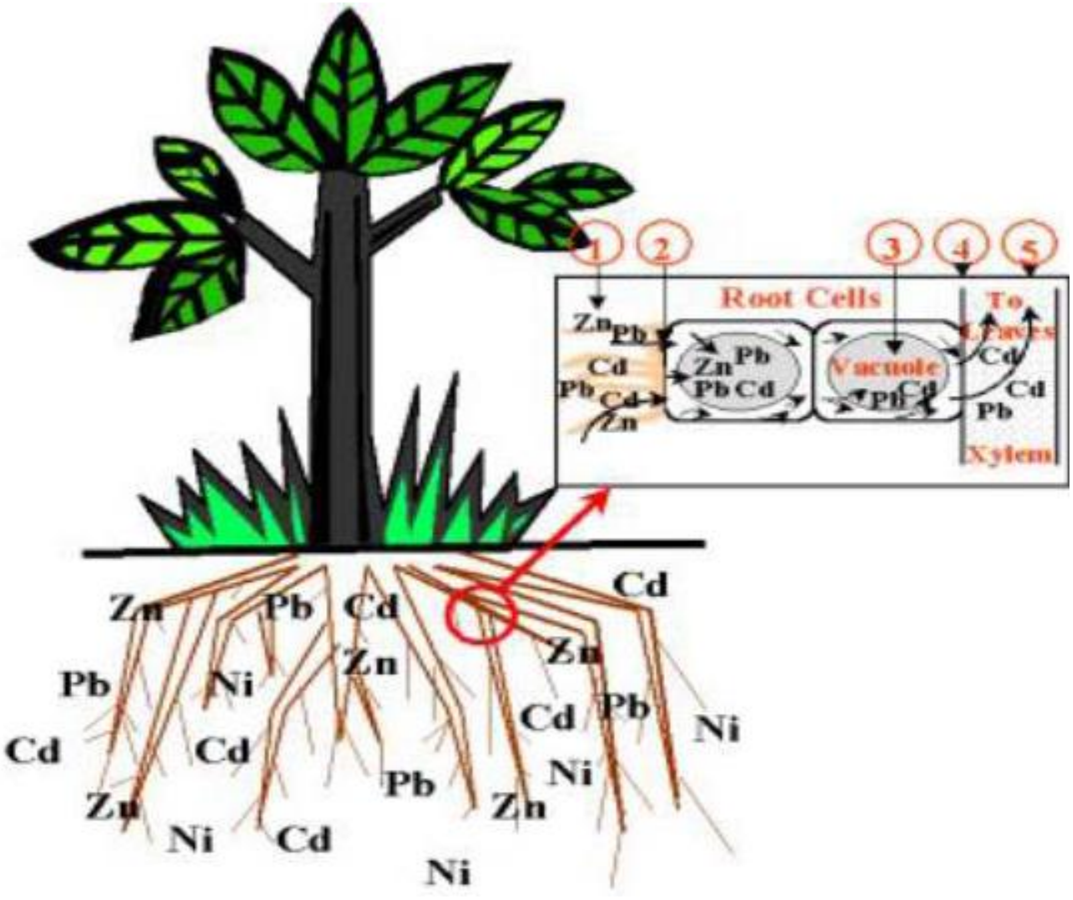


Figure 2.1: The metal uptake and accumulation in plants (Lasat, 2000)

1. A metal fraction is adsorbed at root surface.

2. Bioavailable metal moves across cellular membrane into root cells.

3. A fraction of the metal absorbed into roots is immobilized in the vacuole.

4. Intracellular mobile metal crosses cellular membranes into root vascular tissue (xylem).

5. Metal is translocated from the root to aerial tissues (stems and leaves).

2.9 Health effect of heavy metals

2.9.1 Health effects of Lead

Lead (Pb) poisoning has several symptoms including headache, irritability, abdominal pain, sleeplessness and restlessness; children may be affected by behavioral disturbances, learning and concentration difficulties (Bull, 2003). Lead (Pb) is non- essential element and it is toxic even in trace amount (WHO, 2010). 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). 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).

2.9.2 Health effects of Chromium

Chromium is present in rocks, soil, animals and plants. It can be solid, liquid, and in the form of gas. Chromium compounds are very much persistent in water sediments. They can occur in many different states such as divalent, four-valent, five-valent and hexavalent state. Cr (VI) and Cr (III) are the most stable forms and only their relation to human exposure is of high interest (Zhitkovich, 2005). Chromium (VI) compounds, such as calcium chromate, zinc chromates, strontium chromate and lead chromates, are highly toxic and carcinogenic in nature. Chromium (III), on the other hand, is an essential nutritional supplement for animals and humans and has an important role in glucose metabolism. The uptake of hexavalent chromium compounds through the airways and digestive tract is faster than that of trivalent chromium compounds. Occupational sources of chromium include protective metal coatings, metal alloys, magnetic tapes, paint pigments, rubber, cement, paper, wood preservatives, leather tanning and metal plating (Martin and Griswold, 2009). When broken skin comes in contact with any type of chromium compounds, a deeply penetrating hole will be formed. Exposure to chromium compounds can result in the formation of ulcers, which will persist for months and heal very slowly (Jaishankar *et al.,* 2014). Ulcers on the nasal septum are very common in case of chromate workers. Results obtained from different chromate compounds can induce DNA damage in many different ways and can lead to the formation of DNA adducts, chromosomal aberrations, alterations in replication and transcription of DNA (O'Brien *et al.,* 2001).

2.9.3 Health effects of Cadmium

Cadmium (Cd)) occurs naturally in combined form especially with oxygen, sulphate and chloride. It is a very toxic metal. All soils and rocks, including coal and mineral fertilizers, contain some cadmium (Martin et al., 2009). According to WHO (2010) human exposure occurs mainly through consumption of contaminated food, active and passive inhalation of tobacco smoke and inhalation by workers in the non-ferrous metal industry. Ingesting very high levels severely irritates the stomach, leading to vomiting and diarrhea. Long-term exposure to lower levels leads to a buildup in the kidneys and possible kidney disease, lung damage, and fragile bones (IPCS, 2005–2007). 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 morpho pathological 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).

2.9.4 Health effects of Arsenic

Generally inorganic arsenic is strongly toxic and intake of large quantities leads to gastrointestinal symptoms, severe disturbances of the cardiovascular and central nervous systems, and finally death (Bull, 2003). Arsenic exposure during pregnancy is a particular public health concern due to the additional health risks imposed on the fetus. In epidemiological studies, maternal urinary arsenic (a biomarker of recent exposure) has been related to infant mortality (Karagas *et al.,* 2004) and low birth weight (Rahman *et al.,* 2010). Moreover, in utero arsenic exposure has been linked to hampered immune function (Rahman *et al.,* 2009) and increased mortality from lung cancer later in life (Smith *et al.,* 2006). Given that fetal development is generally a period of heightened vulnerability to environmental toxicants (Brent *et al.,* 2004), it is especially crucial to characterize the sources and extent of arsenic exposure in pregnant women.

2.9.5 Health effects of Copper

Copper (Cu) is an essential nutrient in the human body in trace amount. Excess Cu can result in a number of poor health effect including liver and kidney damage, anemia and developmental toxicity (Brewer, 2010). Copper is an essential nutrient that is incorporated into a number of metal enzymes involved in hemoglobin formation, drug/xenobiotic metabolism, carbohydrate metabolism, catecholamine biosynthesis, the crosslinking of collagen, elastic, and hair keratin, and the antioxidant defense mechanism. Copper-dependent enzymes, such as cytochrome C oxidase, mono oxygenase, function to reduce activated oxygen species or molecular oxygen. Symptoms associated with copper deficiency in humans include normocytic, hypochromic anaemia, leukopenia, and osteoporosis (ATSDR, 2004).

Although copper homeostasis plays an important role in the prevention of copper toxicity, exposure to excessive levels of copper can result in a number of adverse health effects including liver and kidney damage, anemia, immune toxicity, and developmental toxicity. Many of these effects are consistent with oxidative damage to membranes or macromolecules. Copper can bind to the sulfhydryl groups of several enzymes, such as glucose-6-phosphatase and glutathione reductase, thus interfering with their protection of cells from free radical damage (ATSDR, 2004).

There are numerous reports of acute gastrointestinal effects in humans after ingestion of large amounts of copper in drinking water or beverages. The most prevalent effects are nausea and vomiting, which typically occur shortly after ingestion and are not persistent (Araya *et al.*, 2001).

Most of the available human studies examined the relationship between copper exposure and the manifestation of symptoms of gastrointestinal irritation. Gotteland *et al.* (2001) also looked at physiological alterations. Gotteland et al. (2001) found significant increases in gastric permeability to sucrose following the bolus ingestion of 10 ppm copper as copper sulfate (0.03 mg Cu/kg); no alterations in intestinal permeability to lactulose/mannitol were found.

2.9.6 Health effects of Nickel

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 urea 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 ultra structure 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 tumors, while systematic effects whose initial symptoms are mild nausea, headache, 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). Hyper accumulator plants can store high concentration of hazardous metals which may affect the human and animal health through entering in food chain. The consequence of phyto remediation 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 hemicelluloses 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 phyto remediation should be non-edible, disease resistant and can only be used for renewable energy source.

2.9.7 Health effects of 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 side rophility 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 absorbed 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 (Rangel and Solache, 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 has 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).

The presence of Cobalt 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, wheat havs the highest. In vegetables, cabbage and lettuce are characterized by the highest cobalt contents (Kumar *et al.,* 2007).

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. It's very high doses (320 mg Co·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 B12 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 (Cihan *et al.*, 2011; Pietrodangelo et al., 2014).

Basu *et al.* (2010) and Ryuko *et al.* (2012) reported that the most frequent symptoms of cobalt excess are skin inflammations and asthma. Frequent use of tools which contain cobalt add mixtures, 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 it's 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 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).

CHAPTER THREE

MATERIALS AND METHODS

This chapter includes the details of the materials and methods of this research work. The experimental materials, site, collection of samples, experimental designs etc. are described under their headings below. This study was undertaken during the time of June 2022 to April 2023 for the determination of heavy metals in different pesticide samples collected from different cities of Bangladesh.

3.1 Sampling Site and location

Samples were collected from three different places in Bangladesh. They were

1. Monirampur, Jessore
2. Barinagar, Jessore
3. Mithapukur, Rangpur

Figure 3.1: Sampling location

3.2 Collection of pesticide samples

38 samples of different groups were collected randomly from different cities in Bangladesh. Among them some are liquid, some are powdered and some are granular in formation. As the formation of the sample is different so the amounts of them are also different. Some of them are in kilogram, some are in gram and some are in milliliter. Sources and places of collection of pesticide samples are presented in Table 1.

Table 3.1: List of collected pesticide samples with their active ingredients

SL NO.	Product Name	Pesticide Group	Active Ingredient	Formulation	Company Name	Collection Area
01	Dursban	Organophosphate	Chlorpyrifos	20EC	Auto Crop Care Limited	Barinagar, Jessore
02	Morter	Organophosphate	Chlorpyrifos	48EC	National Agri Care Import & Export Ltd	Barinagar, Jessore
03	Starban	Organophosphate	Chlorpyrifos	48EC	Blessing Agrovet Industries Ltd.	Barinagar, Jessore
04	Pioneer	Organophosphate	Chlorpyrifos	48EC	Amco Agricultural Industries	Barinagar, Jessore
05	Gola	Organophosphate	Chlorpyrifos	48 EC	ACI Formulations Limited	Barinagar, Jessore
06	Chlorocel	Organophosphate	Chlorpyrifos	48 EC	Haychem (Bangladesh)	Barinagar, Jessore

					Limited	
07	Fyfanon	Organophosphate	Chlorpyrifos	57 EC	Shetu Agro Industries Limited	Barinagar, Jessore
08	Hilthion	Organophosphate	Chlorpyrifos	57 EC	The Limit Agroproducts Limited	Barinagar, Jessore
09	Malathion	Organophosphate	Chlorpyrifos	57 EC	Alpha Agro Limited	Barinagar, Jessore
10	D-Thion	Organophosphate	Chlorpyrifos	57 EC	Dreamland Agro Products	Barinagar, Jessore
11	G-Thion	Organophosphate	Chlorpyrifos	57 EC	Ekota Agro Products	Barinagar, Jessore
12	Acehero	Organophosphate	Acephate	75 SP	The Limit Agroproducts Limited	Mithapukur, Rangpur
13	Pillarthate	Organophosphate	Acephate	75 SP	Shetu Pesticides Limited	Mithapukur, Rangpur
14	Asataf	Organophosphate	Acephate	75 SP	Auto Crop Care Limited	Mithapukur, Rangpur
15	Basumeal	Organophosphate	Diazinon	10 G	Quality Pest Control	Mithapukur, Rangpur
16	Dianon	Organophosphate	Diazinon	10 G	Shetu Pesticides Limited	Mithapukur, Rangpur
17	Amcozinon	Organophosphate	Diazinon	10 G	Atherton	Mithapukur,

					Imbros Company Ltd.	Rangpur
18	Razdan	Organophosphate	Diazinon	10 G	ACI Formulations Limited	Mithapukur, Rangpur
19	Cyper	Pyrithroid	Cypermethrin	10 EC	General Agro Chemicals Ltd.	Monirampur, Jessore
20	Century	Pyrithroid	Cypermethrin	10 EC	Crop Protection & Care Center	Monirampur, Jessore
21	Magic	Pyrithroid	Cypermethrin	10 EC	Reximco Insecticides Limited	Monirampur, Jessore
22	Genethrin	Pyrithroid	Cypermethrin	10 EC	Genetica Industries Ltd.	Monirampur, Jessore
23	Agromethrin	Pyrithroid	Cypermethrin	10 EC	Shetu Pesticides Limited	Monirampur, Jessore
24	Ripcord	Pyrithroid	Cypermethrin	10 EC	BASF Bangladesh Limited	Monirampur, Jessore
25	Superthrin	Pyrithroid	Cypermethrin	10 EC	SAM Agro Chemical	Monirampur, Jessore
26	kaka	Pyrithroid	Cypermethrin	10 EC	Cobra Agro Care Ltd.	Monirampur, Jessore
27	Gati	Pyrithroid	Cypermethrin	10 EC	Tata Crop Care Company	Monirampur, Jessore
28	Message	Pyrithroid	Cyhalothrin	2.5 EC	Alpha Agro	Monirampur,

					Limited	Jessore
29	Karate	Pyrithroid	Lamda-Cyhalothrin	2.5 EC	Syngenta Bangladesh Limited	Monirampur, Jessore
30	Exit	Pyrithroid	Lamda-Cyhalotrhin	2.5 EC	Atherton Imbros Company Ltd.	Monirampur, Jessore
31	karathrin	Pyrithroid	Lamda-Cyhalothrin	2.5 EC	Aranya Crop Care Limited	Monirampur, Jessore
32	Jubas	Pyrithroid	Lamda-Cyhalothrin	2.5 EC	Intefa	Monirampur, Jessore
33	Canopy Plus	Imidachloprid	Imidacloprid	70 WG	Asia Trade International	Monirampur, Jessore
34	Door	Imidachloprid	Imidacloprid	70 WG	Rural Agro Science	Monirampur, Jessore
35	Ricomire	Imidachloprid	Imidacloprid	70 WG	Padma Agro Sprayers Co.	Monirampur, Jessore
36	Ble-King	Imidachloprid	Imidacloprid	70 WG	Blessing Agrovet Industries Ltd.	Monirampur, Jessore
37	Pinador	Imidachloprid	Imidacloprid	70 WG	Promote Agro Limited	Monirampur, Jessore
38	Marshal	Carbamate	Carbosulfan	20 EC	Auto Crop Care Limited	Monirampur, Jessore

3.3 Sample analysis

3.3.1. Experimental site

The samples were collected from the districts of Rangpur and Jessore. After collecting the samples were prepared for digestion in the Agricultural Chemistry Laboratory in Sher-e-Bangla Agricultural University.

3.3.2 Sample digestion

The most commonly used pesticides in the cultivated areas of some cities were selected. Heavy metals from the samples were extracted by the wet extraction method (AOAC, 1984). A gram of sample was placed in a 100 ml conical beaker to which 20 ml of 70% nitric acid (HNO_3) was added. The digestion was performed on a sand bath at 60 to 80 degree centigrade until the brown gas evaporated. Then, 3 ml of 65% perchloric acid ($HCLO_4$) was added, followed by heating on a sand bath until the mixture was cleared. The cooled mixture was filtered through a 0.45µm Millipore filter paper assisted by vacuum pressure before being transferred into a volumetric flask and made up to 100 ml with distilled water. Sample digestion procedure was completed in the laboratory of Agricultural Chemistry Department of Sher-e-Bangla Agricultural University, Dhaka, Bangladesh.

3.3.3 Analysis

Prepared digested samples were brought to the laboratory. Concentration of heavy metals in the acidic solution was estimated using atomic absorption spectrometry (AAS). Estimations were carried out using the hollow cathode lamps depending upon the element to be tested. The results were expressed as mg/kg.

3.3.4 Standards

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

3.4 Method validation

The digestion method and atomic absorption spectroscopy analysis (AAS; Model-AA-7000) were validated by recovery method. Randomly selected samples were spiked with six different concentrations of heavy metals one at a time (0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 ppm) each run in with the AAS 44 machine. This was followed by the digestion of the spiked 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).

3.5 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.

3.6 Statistical analysis

The experiment was laid out in Completely Randomized Design (CRD). Mean concentrations of heavy metals in pesticides 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).

3.7 Data analysis

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

3.8.1Heavy metal limits

Table 3.2: Allowable limits of heavy metal

Source	Maximum acceptable limit (MAL) mg/L			References
	Lead (Pb)	Chromium (Cr)	Cadmium (Cd)	
Pesticide	0.3	2.3	0.2	FAO/WHO, 2011

3.8.2 Single factor pollution index (PI)

Pollution index 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 Environment Protection Agency (USEPA) Food and Agricultural Organization (FAO) (Jamali et al., 2007).

Mathematically, PI is expressed as:

$PI = C_{Pesticide}/C_{FAO/WHO\text{-}Standard}$

Where,

PI is the individual pollution index of study metal,

$C_{Pesticide}$ is the concentration of the metal in pesticide.

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

3.8.3 Sum of pollution index (SPI)

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

SPI= PIPb+ PICd+ PICr

Where, PI= Single factor index of heavy metals

3.8.4 Metal pollution index (MPI)

To examine the overall heavy metal concentrations in pesticides, 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/L)= $(C_1 \times C_2 \times C_3 \times \ldots\ldots\ldots \times C_n)^{1/n}$

Where, C_n= Concentration of metal n in the sample

Concentration and absorption of standards (0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0) for determination of Pb, Cr and Cd were shown with calibration curves respectively in table and figure 4.1, 4.2 and 4.3.

3.9 Lead concentrations

Table 3.3 Absorption of standard concentration for determination of Pb (Lead)

Concentration	Absorption (mg/L)
0	-0.00467
0.2	0.00840
0.4	0.02222
0.6	0.03218
0.8	0.04488
1.0	0.05660
2.0	0.11696

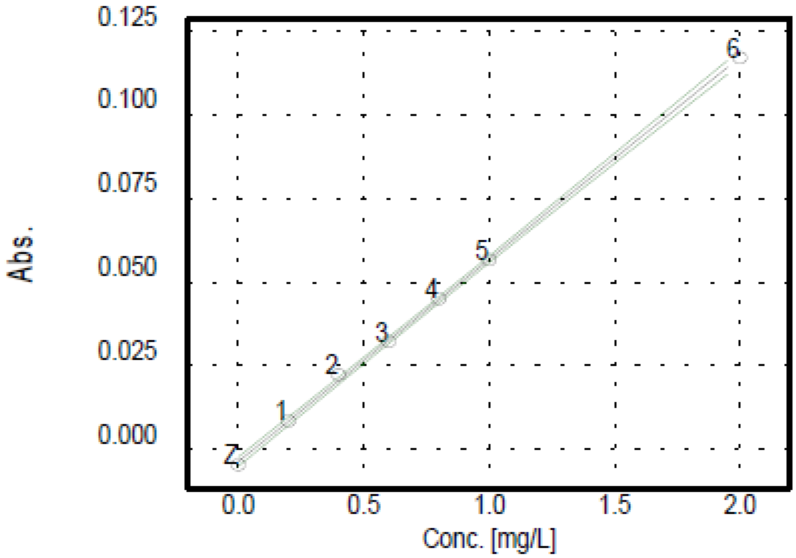


Figure 3.2 Standard calibration curves for determination of Pb (Lead)

3.10 Chromium concentrations

Table 3.4 Absorption of standard concentration for Cr (Chromium)

Concentration	Absorption (mg/L)
0	0.00566
0.2	0.03165
0.4	0.05821
0.6	0.07345
0.8	0.08584
1.0	0.11248
2.0	0.20850

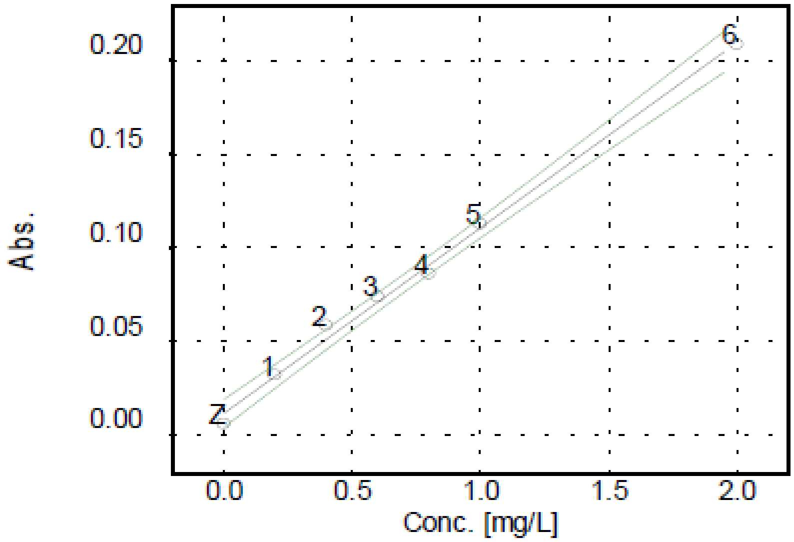


Figure 3.3 Standard calibration curves for determination of Cr (Chromium)

3.11 Cadmium concentrations

Table 3.5 Absorption of standard concentration for determination of Cd (Cadmium)

Concentration	Absorption (mg/L)
0	-0.00130
0.2	0.06223
0.4	0.16690
0.6	0.22974
0.8	0.30544
1.0	0.37287
2.0	0.63496

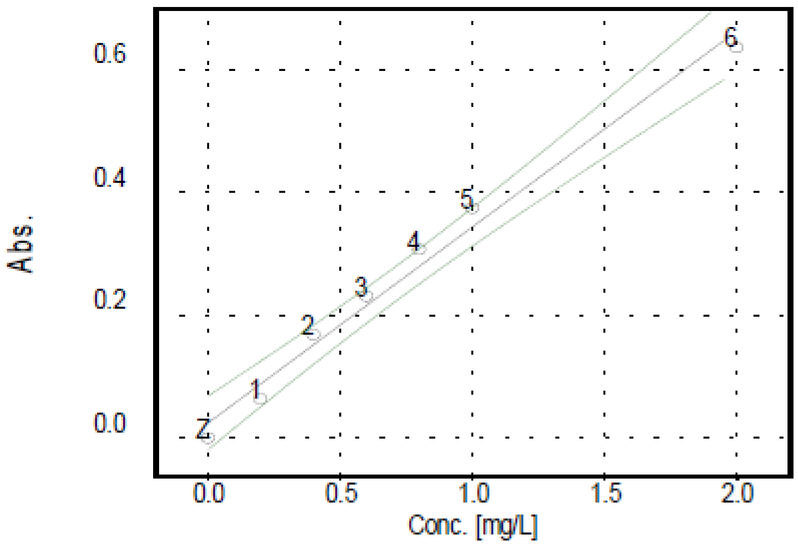


Figure 3.4 Standard calibration curves for determination of Cd (Cadmium)

CHAPTER FOUR

RESULT AND DISCUSSION

This chapter presents heavy metal contents in pesticides mostly uses in different places of Bangladesh. The results were discussed and compared with concentration values reported from other countries and other International standards such as FAO/WHO to assess the safety for human health.

Table 4.1 showed different pesticide samples collected from three different cities (Monirampur, Barinagar and Mithapukur) in Bangladesh containing different detected heavy metal. Total thirty eight samples of different pesticides of four groups (Organophosphate, Pyrithrin, Imidachloprid, Carbamate) were analyzed to find out the heavy metal contamination (Pb, Cr and Cd).

4.1 Lead concentrations in pesticides

Consideration of Pb (Lead) concentration, it was ranging from 0.038 ppm to 0.676 ppm among the pesticide samples collected. Results indicated that the highest Pb concentration (0.676 ppm) was found in the pesticide name Dursban (Organophosphate group) whereas sample (from Pyrithroid group) Jubas showed lowest Pd concentration (0.038 ppm). Maximum allowable concentration of Pb in sampled pesticides under consideration of health risk given by FAO/WHO is 0.3 mg/L which is lower than Pb content in some collected pesticide samples. So, according to FAO/WHO (2011), Pb content in collected pesticide samples might be risky for health in terms of over Pb content. Among 38 samples 14 samples were contaminated with lead (Pb) concentration.

4.2 Chromium concentrations in pesticides

Consideration of Cr (Chromium) concentration, it was ranging from .002 ppm to 1.34 ppm among the pesticide samples. Results indicated that the highest d concentration (1.34ppm) was found in Asataf (organophosphate group) whereas samples Genethrin (Organophosphate group) showed lowest Cr concentration (0.002 ppm). Maximum allowable concentration of Cr in sampled pesticide consideration of health risk given by FAO/WHO is 2.3 mg/L which is higher than Cr content in collected pesticide samples. So, according to FAO/WHO (2011), Cr content in collected pesticide samples might not be risky for health in terms of over Cr content.

4.3 Cadmium concentrations in pesticides

Consideration of Cd (Cadmium) concentration, it was ranging from -0.05 ppm to -0.01 ppm among the pesticide samples. Results indicated that the highest Cd concentration (-0.01ppm) was found in Pinador (Imidachloprid group) whereas samples G-Thion (Pyrithroid group) showed lowest Cd concentration (-0.05 ppm). Maximum allowable concentration of Cd in sampled pesticide consideration of health risk given by FAO/WHO is 0.2 mg/L which is higher than Cd content in collected pesticide samples. So, according to FAO/WHO Cd content in collected pesticide samples might not be risky for health in terms of over Cd content.

Table 4.1 Heavy metal concentration in collected pesticide samples from three different cities in Bangladesh.

Name of Pesticide	Level of heavy metals (ppm)		
	Lead (Pb)	Cromium (Cr)	Cadmium (Cd)
Dursban	**0.676***	0.295	<0.042
Morter	**0.467***	<0.159	<0.039
Starban	**0.409***	<0.781	<0.047
Pioneer	**0.435***	<0.057	<0.048
Gola	**0.426***	<0.007	<0.047
Chlorocel	**0.416***	<0.027	<0.046
Fyfanon	**0.361***	<0.028	<0.045
Hilthion	**0.348***	<0.020	<0.041
Malathion	**0.386***	0.004	<0.041

D-Thion	**0.320***	<0.001	<0.049
G-Thion	**0.385***	0.063	<0.050
Acehero	**0.313***	0.293	<0.026
Pillarthate	0.211	0.739	<0.038
Asataf	0.155	1.34	<0.036
Basumeal	0.218	0.011	<0.027
Dianon	0.193	0.153	<0.022
Amcozinon	0.226	0.191	<0.018
Razdan	0.180	0.086	<0.016
Cyper	0.300	<0.146	<0.039
Century	0.263	<0.010	<0.047
Magic	0.242	0.022	<0.042
Genethrin	0.230	0.002	<0.044
Agromethrin	0.234	<0.011	<0.039
Ripcord	0.233	<0.034	<0.019
Superthrin	0.295	0.064	<0.042
kaka	0.211	0.014	<0.039
Gati	0.188	<0.011	<0.044
Message	0.196	0.081	<0.036
Karate	0.170	0.256	<0.038
Exit	0.126	0.673	<0.041
karathrin	0.073	1.194	<0.039

Jubas	0.038	<0.087	<0.035
Canopy Plus	0.152	<0.014	<0.028
Door	0.137	<0.024	<0.026
Ricomire	0.152	<0.015	<0.023
Ble-King	0.124	0.013	<0.027
Pinador	0.147	0.042	<0.010
Marshal	0.092	0.020	<0.030

[Note: * sign indicates the above limit of heavy metal concentration]

4.4 The single factor pollution index (PI)

The single factor 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 Food and Agricultural Organization (FAO), World Health Organization (WHO), United States Environmental Protection Agency (USEPA). Values of PI<1 indicates that the material is not yet contaminated, whereas PI>1 indicates pollution. On the other hand, PI=1 reveals a critical state which makes the involved samples useful for environmental monitoring (Chukwuma, 1994). In terms of collected pesticide samples from different groups organophosphate group is contaminated (PI>1) in terms of contamination, whereas the groups of imidachloprid and carbamate are not yet contaminated (PI<1). In pyrithroid group one sample is contaminated and others are not.

Table 4.2 Single factor pollution index (PI), sum of pollution index (SPI) and metal pollution index (MPI) of four groups (Organophosphate, Pyrithroid, Imidachloprid and Carbamate)

Pesticides	Single factor pollution index (PI)			Sum of pollution index	Metal pollution index
	Pb	Cr	Cd	SPI	MPI
Dursban	2.25	0.12	0.21	2.58	0.206
Morter	1.55	0.06	0.19	1.8	0.144
Starban	1.36	0.33	0.23	1.92	0.250
Pioneer	1.45	0.02	0.24	1.71	0.106
Gola	1.42	0.003	0.23	1.65	0.047
Chlorocel	1.38	0.01	0.23	1.62	0.081
Fyfanon	1.20	0.01	0.22	1.43	0.076
Hilthion	1.16	0.008	0.20	1.36	0.060
Malathion	1.28	0.001	0.20	1.4	0.040
D-Thion	1.06	0.0004	0.24	1.3	0.022
G-Thion	1.28	0.02	0.25	1.55	0.102
Acehero	1.04	0.12	0.13	1.29	0.129
Pillarthate	0.70	0.34	0.19	1.23	0.174
Asataf	0.51	0.58	0.18	1.27	0.194
Basumeal	0.72	0.004	0.13	0.72	0.040
Dianon	0.64	0.06	0.11	0.81	0.086

Amcozinon	0.75	0.08	0.09	0.92	0.091
Razdan	0.60	0.03	0.08	0.71	0.060
Cyper	1	0.06	0.19	1.25	0.102
Century	0.87	0.004	0.23	1.10	0.047
Magic	0.80	0.009	0.21	1.01	0.060
Genethrin	0.76	0.0008	0.22	0.98	0.028
Agromethrin	0.78	0.004	0.19	0.97	0.047
Ripcord	0.77	0.01	0.09	0.87	0.047
Superthrin	0.98	0.02	0.21	1.21	0.095
kaka	0.70	0.006	0.19	0.89	0.047
Gati	0.62	0.004	0.22	0.84	0.046
Message	0.65	0.03	0.18	0.85	0.081
Karate	0.56	0.11	0.19	0.86	0.102
Exit	0.42	0.29	0.20	0.91	0.147
karathrin	0.24	0.51	0.19	0.94	0.147
Jubas	0.12	0.03	0.17	0.32	0.047
Canopy Plus	0.50	0.006	0.14	0.65	0.038
Door	0.45	0.01	0.13	0.59	0.044
Ricomire	0.50	0.006	0.11	0.61	0.038
Ble-King	0.41	0.005	0.13	0.54	0.035
Pinador	0.49	0.03	0.05	0.57	0.040
Marshal	0.30	0.08	0.15	0.53	0.038

In terms of collected pesticide samples, among 18 samples of Organophosphate group 12 samples are contaminated and 6 samples are not contaminated in terms of Pb contamination. But all the samples of Organophosphate group are not yet contaminated (PI<1) in terms of Cr and Cd contamination (Figure 4.1).

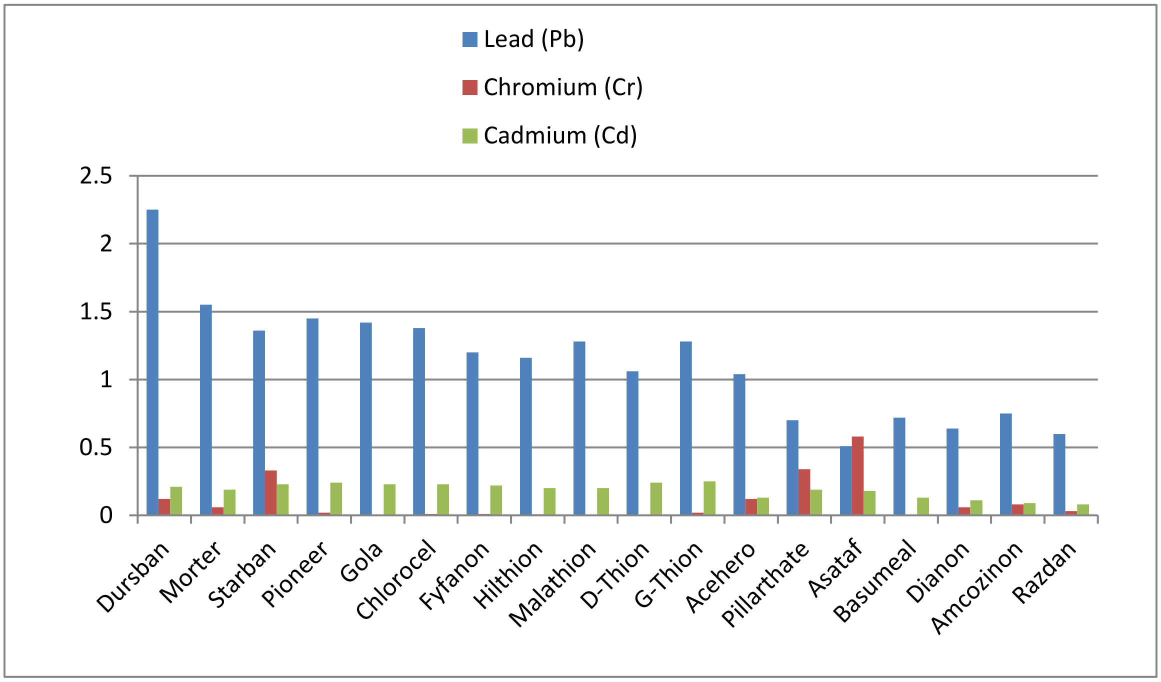


Figure 4.1 Single factor pollution index (PI) for the samples of Organophosphate group

In terms of collected pesticide samples of Pyrithroid group one sample Cyper is in a critical state (PI=1) in term of Pb contamination and others are not yet contaminated (PI<1) in terms of Pb, Cr and Cd contamination (Figure 4.2). So, the selected pesticide collection of this group is safe for the environment except one sample.

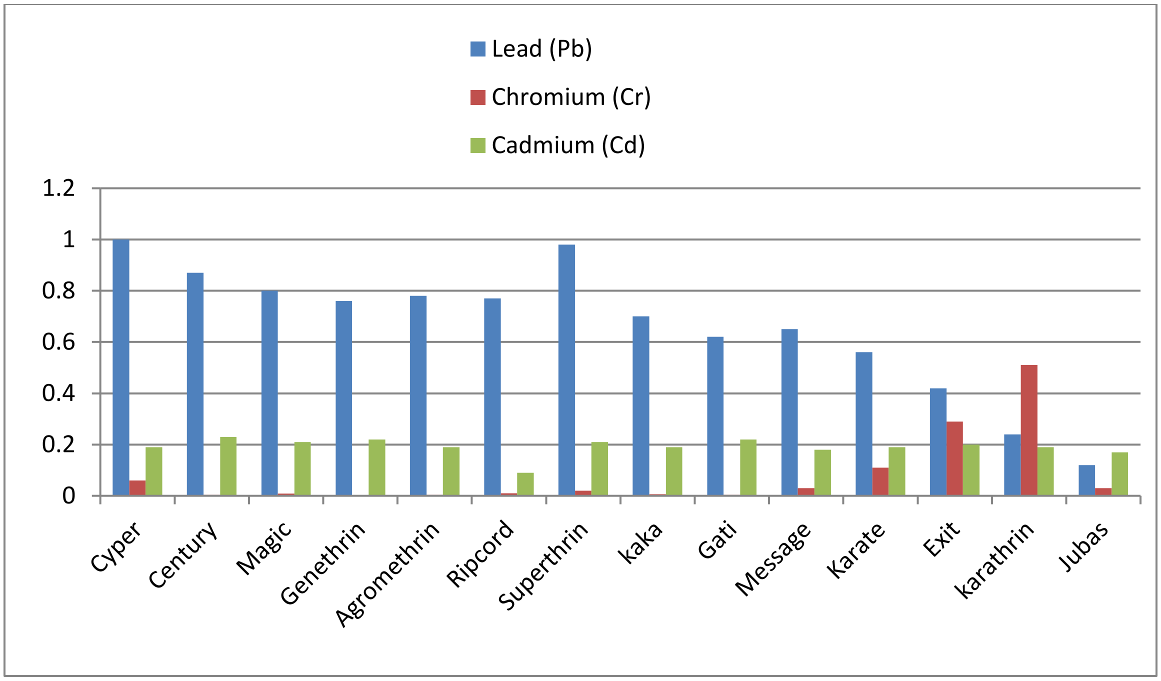


Figure 4.2 Single factor pollution index (PI) for the samples of Pyrithroid group

Collected pesticide samples of Imidachloprid group are not yet contaminated (PI<1) in terms of Pb, Cr and Cd contamination (Figure 4.3). So, the selected pesticide collection of this group is safe for the environment.

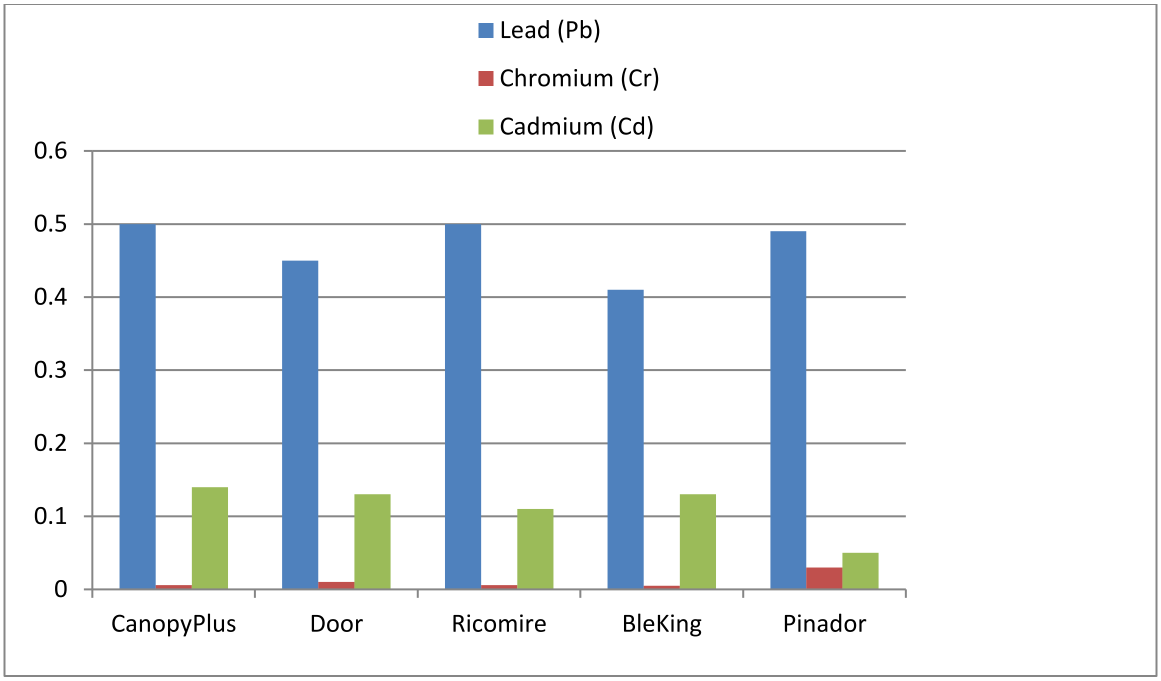


Figure 4.3 Single factor pollution index (PI) for the samples of Imidachloprid group

In terms of collected pesticide samples of Carbamate group are not yet contaminated (PI<1) in terms of Pb, Cr and Cd contamination (Figure 4.4). So, the selected pesticide collection of this group is safe for the environment.

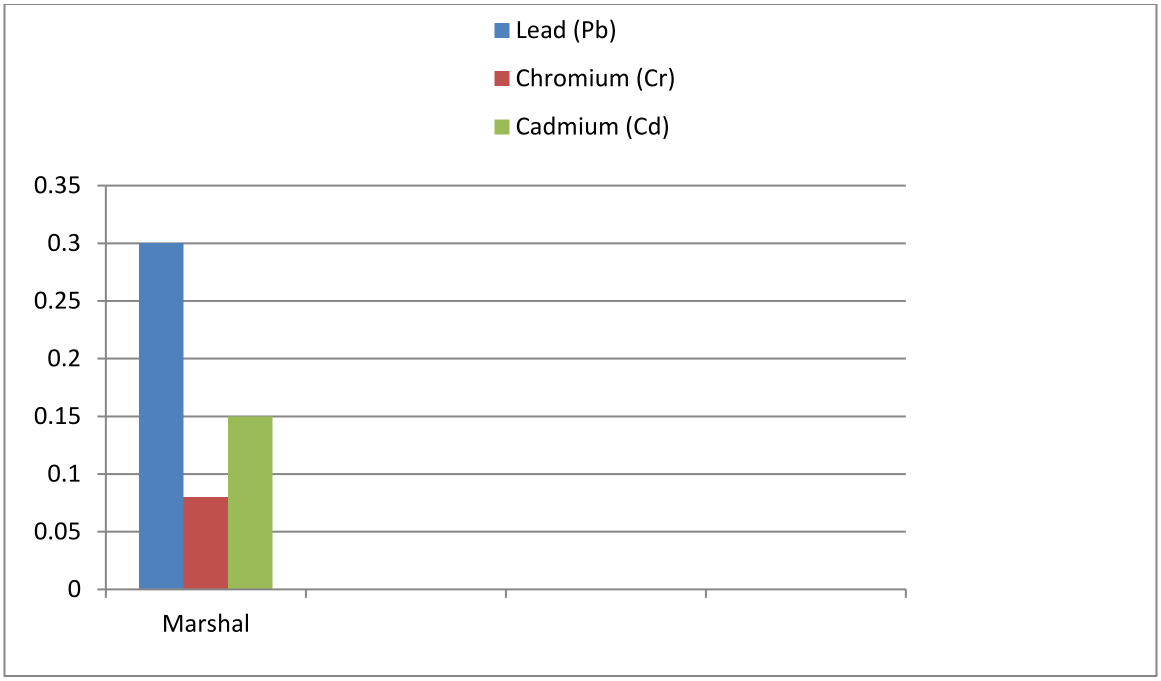


Figure 4.4 Single factor pollution index (PI) for the samples Carbamate group

4.5 Sum of pollution index (SPI)

Sum of pollution index showed little variation in different collected pesticide samples of different groups (Table 4.2). Results showed that the highest SPI (2.25) was in Dursban of Organophosphate group followed by Pyrithroid group (1.25) in Cyper, Imidachloprid group (0.87) in Canopy Plus and Carbamate group (0.53) in Marshal.

4.6 Metal pollution index (MPI)

From different collected samples (Table 4.2) the highest MPI (0.250) was in Starban of Organophosphate group and D-Thion showed the lowest MPI (0.022). In Pyrithroid group the highest MPI (0.147) was found in both Exit and Karathrin whereas the lowest MPI (0.028) was found in Genethrin. In Imidachloprid group the highest MPI (0.044) was found in Door and the lowest MPI (0.035) was found in Ble-king. MPI (0.038) was found in Marshal of Carbamate group.

CHAPTER FIVE

SUMMURYAND CONCLUSION

The study was carried out at the Laboratory of Agricultural Chemistry Department Sher-e-Bangla Agricultural University, Sher-e-Bangla Nagar, Dhaka, during the time June 2022 to April 2023 for the determination and risk analysis of heavy metals in different samples collected from different places in Bangladesh. Three places (1) Monirampur, Jeshore, (2) Barinagar, Jeshore, (3) Mithapukur, Rangpur were selected for sample collection. Samples were collected on four groups namely (i) Organophosphate, (ii) Pyrithroid, (iii) Imidachloprid and (iv) Carbamate. So, thirty eight unit samples were considered for the present study. Samples were analyzed to determine lead (Pb), chromium (Cr) and cadmium (Cd) using the 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 pesticide samples of Organophosphate group the highest Pb (0.676 ppm) was found in Dursban, highest Cr (1.34 ppm) was found in Asataf and highest Cd (0.05 ppm) was found in G-Thion. Similarly, Asataf sample showed lowest Pb concentration (0.155 ppm) whereas the lowest Cr and Cd concentration (0.001 ppm and 0.026 ppm respectively) were found from D-Thion and Acehero.

In terms of different pesticide samples of Pyrithroid group the highest Pb concentration (0.30 ppm) was found in Cyper, highest Cr (1.194 ppm) was found in Karathrin and highest Cd (0.047 ppm) was found in Century. Similarly, sample Jubas (0.038 ppm) showed lowest Pb concentration whereas the lowest Cr concentration (0.002 ppm) found in Genethrin and lowest Cd concentration (0.019 ppm) was found in Ripcord.

Considering different pesticide samples of Imidachloprid group the highest Pb concentration (0.152 ppm) were found in Canopy plus and Ricomyar also, the highest Cr concentration (0.042 ppm) was found in Pinador and highest Cd concentration (0.028 ppm) was found in Canopy Plus. Similarly, the lowest Pb and Cr concentration (0.124 ppm and 0.013 ppm respectively) was found in Ble-king, sample Pinador showed the lowest Cd concentration (0.010 ppm).

In terms of pesticide samples of Carbamate group Marshal showed the Pb concentration 0.092 ppm, Cr concentration 0.020 ppm and Cd concentration 0.030 ppm.

Regarding pollution index (PI), all collected samples of Organophosphate group were in PI>1 which indicates that the samples are contaminated in respect of heavy metal content except two samples Pillarthate and Asataf (PI=0.70) in terms of Pb concentration. But all the samples of Organophosphate group are not yet contaminated (PI<1) in terms of Cr and Cd contamination. Similarly, samples of Pyrithroid group one sample Cyper is in a critical state (PI=1) in term of Pb contamination and others are not yet contaminated (PI<1) in terms of Pb, Cr and Cd contamination. Rest of the samples of group Imidachliprid and Carbamate are not yet contaminated (PI<1) in terms of Cr and Cd contamination.

In case of sum of pollution index (SPI), the highest SPI (2.58) was in Dursban of Organophosphate group and the lowest SPI (0.32) was in Jubas of Pyrithroid group. Again considering metal pollution index (MPI), the highest MPI (0.250) was in Starban of Organophosphate group and the lowest MPI (0.022) was in D-Thion.

Recommendation

From the above result, therefore reported that heavy metals in pesticide samples of the study groups some were higher than and some were below safe limit approved by FAO/WHO. So, further study can be conducted in other groups of pesticides to justify the present study.

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APPENDICES

Appendix I. Result of pesticide samples of Bangladesh Agriculture Research Institute

SL NO.	Name of Pesticide	Lead (Pb)	Cadmium (Cd)	Chromium (Cr)
1	Sanoskinil	2.99	0.189	6.25
2	Micra	4.98	0.06	17.88
3	Suspend	0.001	0.001	2.04
4	Kartalf	0.001	0.002	6.73
5	Nitro	0.54	0.002	2.7
6	Limida	0.33	0.001	1.05
7	Proclaim	0.39	0.001	1.56
8	Volium Flexi	0.3	0.001	2.61
9	Likar	0.81	0.001	2.46
10	Sharper	0.6	0.001	3.24
11	Amistar Top	1.56	0.12	0.18
12	Emitaf	1.62	0.12	0.24
13	Ambush	1.68	0.06	2.64
14	Ecomethrin	1.56	0.18	2.16
15	Uperclam	1.8	0.06	6.06
16	Altimaplus	1.44	0.06	16.02
17	Ecotap	0.84	0.12	9.6
18	Ridomild Gold	1.40	0.12	4.9

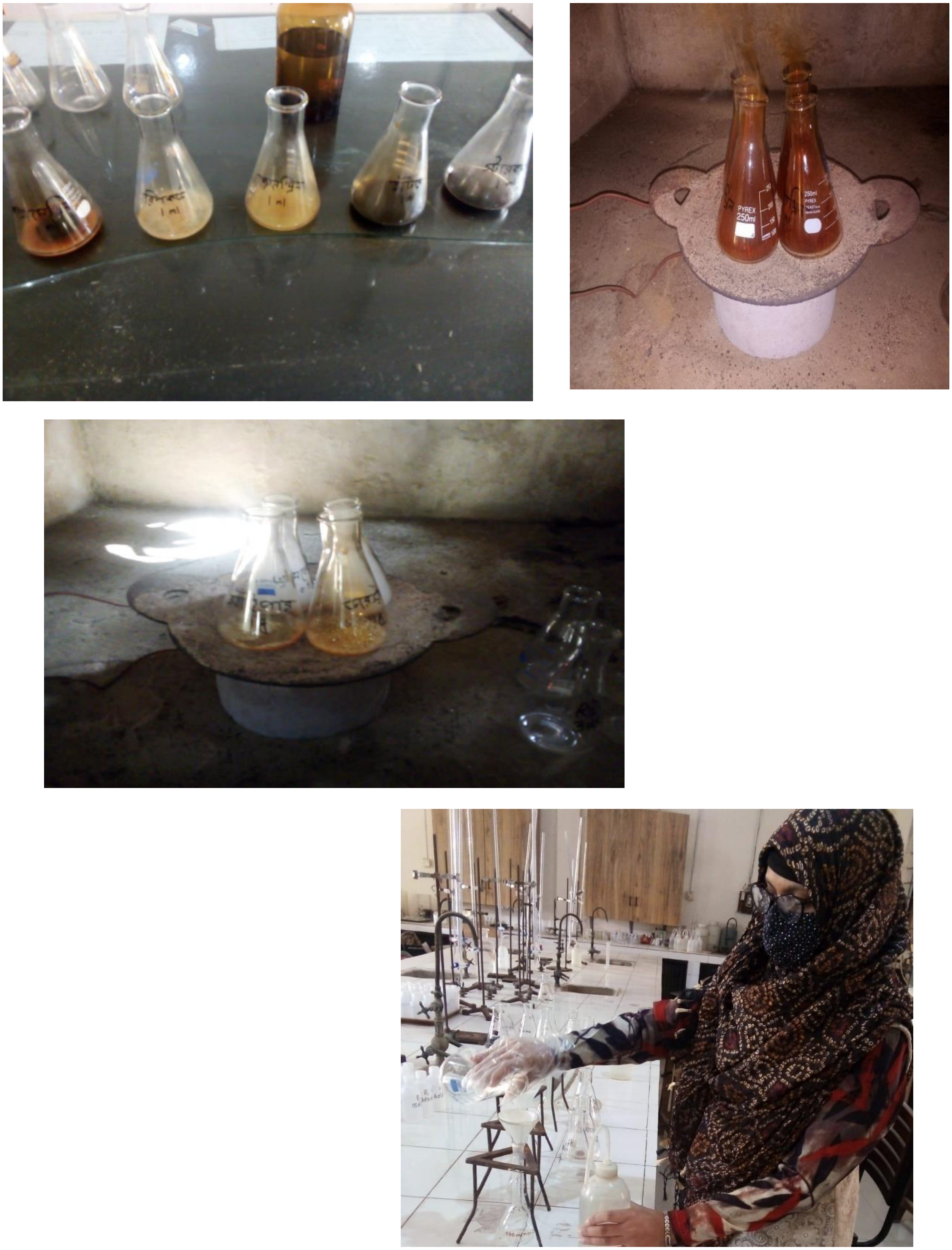
19	Ripcord	0.35	0.03	2.58
20	Knowin	1.32	0.06	5.04
21	Autosin	0.01	0.01	2.4
22	Actara	0.24	0.01	1.98
23	Sunfuran	4.62	0.06	13.98
24	Forwafuran	0.06	0.06	17.76
25	Dursban	0.001	0.06	13.8
26	Vitafuran	o.57	0.06	20.46
27	Irad	0.9	0.12	2.34
28	Optimus	0.01	0.02	17.7
29	Carbotaf	0.01	0.01	12.3
30	Brifur	5.29	0.02	24.66
31	G-mac	0.01	0.06	3.6
32	Copper	1.56	0.06	29.94
33	Usteed	0.06	0.02	0.6
34	Tilt	0.06	0.06	0.24
35	Sevin	3.91	0.12	2.04
36	Fana	1.32	0.06	11.4
37	Gain	0.12	0.01	1.32
38	Acmix	0.9	0.06	3.3
39	Sabion	0.59	0.18	2.22
40	Cotan	0.01	0.01	2.28

41	Setara	0.15	0.12	3.42
42	Sico	0.06	0.12	3.06
43	Surate	0.01	0.01	1.08
44	Metataf	1.8	0.06	44.3
45	Mimtap cartap	0.01	0.01	7.56
46	Cube	1.27	0.12	4.14
47	Wonder	0.01	0.02	4.56
48	Spike	0.01	0.01	5.28
49	Protect	0.01	0.01	3.36
50	Mimfuran	0.56	0.06	20.4
51	Ecofuran	0.18	0.01	12.48
52	Ripcord	0.01	0.01	1.2
53	Ectara	0.18	0.06	2.34

Appendix II. Result of pesticide samples of Atomic Energy Centre

SL NO.	Name of Pesticide	Lead (Pb)	Cadmium (Cd)	Chromium (Cr)
1	Sanoskinil	0.86±0.09	1.18±0.12	1.15±0.12
2	Micra	<0.2	0.63±0.06	2.05±0.20
3	Suspend	<0.2	<0.06	1.10±0.11
4	Kartalf	<0.2	<0.06	4.58±0.46
5	Nitro		<0.06	7.60±0.76
6	Limida	<0.2	<0.06	2.29±0.23
7	Proclaim	<0.2	<0.06	<0.7
8	Volium Flexi	<0.2	<0.06	<0.7
9	Likar		<0.06	<0.7
10	Sharper	<0.2	<0.06	2.10±0.21
11	Amistar Top		<0.06	<0.7
12	Emitaf	<0.2	<0.06	<0.7
13	Ambush	2.26±0.23	<0.06	<0.7
14	Ecomethrin	1.18±0.12	<0.06	0.84±0.08
15	Uperclam	0.71±0.07	<0.06	<0.7
16	Altimaplus	2.06±0.21	<0.06	5.47±0.55
17	Ecotap	2.75±0.28	<0.06	3.55±0.35
18	Ridomild Gold	2.33±0.23	1.15±0.12	1.46±0.15

Sample preparation and digestion



Sample preparation and digestion