ESTIMATION AND HEALTH RISK ASSESSMENT OF SELECTED HEAVY METALS (Cd, Cr, Pb, Cu and Ni) IN CHILDREN TOYS

By

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Thesis submitted to Lahore School of Economics in fulfilment of the requirements for the degree of MPhil in Environmental Science and Policy

2020- 2023

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ABSTRACT

The potential risk that heavy metals cause during the early stages of childhood development makes it a global health concern. Main aim of this study is to determine the concentration of cadmium, chromium, nickel copper, and chromium (VI) to carry out dose response assessment, evaluating questionnaire responses given by children's parents in Lahore, Pakistan and calculating hazard quotient (HQ) in order to evaluate whether concentrations are above or below permissible limit. The concentrations detected by AAS in digested samples ranged from 83.7 mg/kg to -0.087 mg/kg for Cd, 806 mg/kg to -0.05 mg/kg for Cr (VI), 1001 mg/kg to -0.008 mg/kg for Pb, 822 mg/kg to -0.07 mg/kg for Cu, and 3000 mg/kg to -0.9 mg/kg for Ni. 40% samples for Cd, 5% samples for Cr (VI), 55% samples for Pb, and 5% samples for Ni exceeded the EU limit. Based on the HQ values detected, trend of concentration of heavy metals exceeding EU regulations was Pb > Cd > Cr (VI) > Ni. Copper did not exceed any regulation yet present in considerable amount of samples. On the basis of data from questionnaire responses and dose response assessment using hazard quotient, heavy metal poisoning has been confirmed as a significant hazard due to the fact that there are a number of health problems linked with it. Once heavy metals get into the living organisms, and the organism is exposed many times heavy metals are bio accumulated and hence it can be harmful to mental health and functioning of the central nervous system.

DEDICATION

I dedicate this thesis to my parents who put so much effort to make me stand here and confident enough to carry out this work.

ACKNOWLEDGEMENT

All praise and thanks to Allah Almighty who gave me courage and strength to complete this thesis.

We would like to thank each person of our department who facilitated us a lot in conducting this research work.

A special thanks that comes in this regard is to my Supervisor Prof. Dr. M. Nawaz Chaudhry and Co-Supervisor Dr Naqi Hussain, because this research could not have been done without their unmatched support and assistance. I appreciate the encouragement and support and inspiration I received from all of my teachers, coworkers, and fellow students. I want to express my gratitude to Lahore School of Economics for giving me the chance to earn an MPhil Scholar degree from this institution. I also acknowledge the CREB Committee because their comments allowed me to refine my research. I thank each and every respondent who took part in this study. Last but not least, I want to express my gratitude to my loved ones for their never-ending prayers and support.

TABLE OF CONTENTS

Abstract i
Dedication ii
Acknowledgement iii
Table of Contents iv
List of Tables vi
List of Figures vii
Abbreviations ix
Chapter 1 1
INTRODUCTION 1
1.1 Exposure of Heavy Metals 1
1.2 Toys Representation of Childhood Amusement 1
1.3 Use of Metal Stabilizers 2
1.4 Dependence of Metal Toxicity 2
1.4.1 Toxicity of Lead 2
1.4.2. Toxicity of Cadmium 3
1.4.3. Toxicity of Chromium (VI) 3
1.4.4. Toxicity of Nickel 3
1.4.5. Toxicity of Copper 4
1.5 Human health Risk Assessment of Heavy Metals 4
1.6. Research Questions 5
Chapter 2 7
LITERATURE REVIEW 7
Chapter 3 14
METHODOLOGY 14
3.1 Desk Study 14
3.2 Review of Previous Research Work 14
3.3 Questionnaire Formation and Analysis 14
3.4 Sample Collection 15
3.5 Determination of total Metal Concentration [Ni, Cu, Cd, Pb, and Cr (VI)] in Toy Samples 16
3.5.1. Preparation of Samples 16

3.5.2, Digestion and Dilution of Samples 17
3.5.3. Detection of Total Heavy Metal Concentration in AAS 19
3.5.3.1. Standards Preparation 20
3.5.3.2: Analysis of Samples 20
3.6. Permissible limit of heavy metal concentration 21
3.7. Health Risk Assessment Study 22
3.8 Non-Carcinogenic Dose Response Assessment 22
3.9. Statistical Analysis 25
Chapter 4 26
RESULTS AND DISCUSSION 26
4.1. Results 26
4.1.1.1. Cadmium 26
4.1.1.2. Chromium (VI) 28
4.1.1.3. Lead 31
4.1.1.4. Copper 33
4.1.1.5. Nickel 35
4.1.2. Exposure Evaluation by filling Questionnaire survey: 39
4.1.3. Dose-Response Assessment 44
4.2. Discussion 47
CONCLUSION 48
REFERENCES 49
APPENDICES 53

LIST OF TABLES

Table 3.1.	Samples labelled with sample codes	16
Table 3.2.	Permissible limit of heavy metal concentration set by Canada (Gov. of Canada 2011, 2018).	21
Table 3.3.	Permissible limit of heavy metal concentration set by United States (US CPSC) (ASTM International 2017) and BIS (Bureau of Indian Standard).	22
Table 3.4.	Input Parameters for Average Daily Dose	24
Table 3.6.	Reference Dose (RfD) for oral consumption associated with non-carcinogenic risks.	24
Table 4.1.	Concentration of Cadmium in 20 samples	27
Table 4.2.	Concentration of Chromium in 20 samples	29
Table 4.3.	Concentration of Lead in 20 samples	31
Table 4.4.	Concentration of Copper in 20 samples	44
Table 4.5.	Concentration of Nickel in 20 samples	46
Table 4.6.	Table 4.7: Exposure Evaluation by filling Questionnaire. Table 4.8:	42
Table 4.7.	Average daily doses of ingestion (ADD) in mg/kg/day and hazard quotient (HQ) in baby toys.	46

LIST OF FIGURES

Figure 3.1	Location of samples collected from various local shops in Lahore, Pakistan.	15
Figure 3.2.	Prepared samples after crushing into small pieces of size of 0.5 cm	17
Figure 3.3.	Samples after dilution	18
Figure 3.4.	Blank solution run on instrument	19
Figure 3.4	Samples detection on atomic absorption 35	19
Figure 4.1.	Concentration of cadmium in selected children toys.	31
Figure 4.2.	Concentration of Cr (VI) in selected children's toys.	33
Figure 4.3.	Concentration of Lead in selected children's toys	35
Figure 4.4.	Concentration of Cu in selected children's toys	37
Figure 4.5.	Concentration of Ni in selected children's toys.	38
Figure 4.6.	Maximum to minimum concentration of heavy metals in children's toys.	38
Figure 4.7.	Fig 4.7. Samples (n=20) exceeding EU, US, Canadian and BIS regulation.	38
Figure 4.8.	.Questionnaire responses to sickness due to toys.	44
Figure 4.9.	Hazard Quotient of heavy metals	46

ABBREVIATIONS

USEPA	United States Environmental Protection Agency
WHO	World Health Organization
AAS	Atomic absorption spectrophotometer
EPA	Environmental Protection Agency
ICP-MS	Inductively coupled plasma mass spectrometry
SEM	Scanning Electron Microscopy
Dderm	Average daily dose (Exposure Dose) via dermal absorption (mg/kg/day).
Csample	Heavy Metal Concentration in sample (mg/l)
SA	Average Surface Area of Scalp (cm2)
Kp	Permeability Coefficient of Heavy Metal
ET	Exposure Time (hours/day)
EF	Exposure Frequency (days/year)
ED	Exposure Duration (year)
BW	Body Weight (kg)
AT	Averaging Time
SSA	Surface Area of Scalp
MTDI	Maximum tolerable daily intake
HQ	Hazard Quotient

Chapter 1

INTRODUCTION

Heavy metals are naturally occurring having a high atomic weight and a density of at least 5 times that of water, or greater than 4 g/cm3. On the basis of atomic masses, density, physical, and chemical toxicity, there are numerous definitions of heavy metals in the literature. The heavy metals consist of lanthanides, actinides, transition metals and some metalloids. They can be hazardous or harmful even at small concentrations, cannot be metabolized by the organism, results in metal body burden, and causes metal deposition (Yang and Massey 2019). (Lenntech, 2004).

Study of heavy metals is known as heavy metals science. Research and development in this domain is not a new field of science; it has been going on for more than a century (Suparna kumar Das, Ajmer singh Grewal, & Mrityunjay, 2011). Most of the heavy metals may ultimately be noxious and even lethal when exposed to human body via ingestion, inhalation or absorption. Determination of toxicity of metals in living organisms is an important issue to consider in the field of agriculture, food, protection of environment and materials of premium quality (Mustafa Soylak, SibelSaraçoğlu, MustafaTüzen, & DuraliMendil, 2005),(Muwaffak Al osman, Fei Yang, & Isaac Yaw Massey, 2019).

1.1 Exposure of Heavy Metals

Exposure of human beings to heavy metals is an important problem of the modern world. Even young children are exposed to these metals through multiple pathways i.e. atmosphere, water, eatables and soil (Guney and Zagury 2013).Due to developmental and physiological growth of young children i.e. high metabolic rate, low body mass and fast_growth rate, they are highly sensitive and vulnerable to various health issues either carcinogenic or non-carcinogenic after having contact with items contaminated with various metals or chemicals (Becker, 2010).

1.2 Toys Representation of Childhood Amusement

Toys are basically artificial representatives of animals, items and people that children can hold and use to play and feel amazed. For toddlers and young children, most of the metal exposure is through toys (Yerkes, 1986). During development of children from early stage of life to teenage, playing with toys is an essential component. Every age group of children play with toys with different styles. This leads to exposure of heavy metals via chewing, licking, sucking or ingestion that results in leaching of heavy metals through saliva from toys (Abhay and Prashant, 2007; Kelly et al, 1993). Once ingested, these metals could be released by the saliva and fluids of intestine and get absorbed in the digestive system of the body. A child's digestive system has ability to absorb around fifty percent of lead after ingesting (Dsouza, 2009).

1.3 Use of Metal Stabilizers

Toys are composed of numerous materials i.e. wood, paints, metals, paint coating and plastics. Plastic Toys comprising polyvinyl chloride (PVC) are commonly used. Polyvinyl chloride is commonly used in soft toys of children e.g. toys in bath, squeezing toys and teething accessories (Tripathy, 2007). Plastic toys contain a wide range of additives in order to plasticize, stabilize, cure, antioxidize and color the products. Stabilizers are utilized to give stability, flexibility, softness and bright colors to toys (Abhay and Prashant, 2007).

Addition of metal stabilizers in toys is essential because they consist of chlorine that forms hydrochloric acid after reaction with free hydrogen ions resulting in degradation of the product if these metal stabilizers are not used in manufacturing. For instance, **Lead (Pb)** effectively bound with chlorine. Chlorine could degrade the product during process while lead stabilizes that product (Greenway, 2010). Since restrictions on lead were put in place through regulations of lead, **cadmium** was substituted as an alternative (A. Kumar, 2007). Zinc (Zn) is usually added with cadmium (Cd) and other metals could be used as pigments to color the plastic products (M. Hillyer, 2014).

1.4 Dependence of Metal Toxicity

Factors affecting toxicity of metals is on interaction of elements, compounds or complex formation in metalloids, their properties either physical or chemical, metals interchange into protiens, source and sink properties of metals, ability of metals to transport and transform in environment, impact of amount and exposure variables of metals including bioavailability, route, pattern and time of exposure, status of nutrition i.e. drugs (nicotine, alcohol etc.) (Żukowska, J, 2008).

1.4.1 Toxicity of Lead

Lead is a potential carcinogenic heavy metal that has significant impact on every organ of the body. High concentration of lead can lead to intense kidney and brain damage which sooner or later may cause death. Lead has been reported to be stored in the bony structures of human beings e.g. teeth and bones and then bio accumulate to further significantly affect the liver and kidneys (WHO 2018).

Lead exposure via absorption in skin is unusual but most susceptible age group is children due to their repeated mouthing and swallowing things containing lead. Such things consist of lead in the form of paint coatings on toys, chips and furniture (He et al, 2009).

Its exposure has been linked with the problems related to emotional and behavioral changes in children. (Even et al, 2015) has reported inattentive, hyper performance and irritating behavior of children who are exposed to lead.

1.4.2. Toxicity of Cadmium

Cadmium and its compounds are carcinogenic in nature. High concentration through ingestion can have adverse impact on the stomach e.g. diarrhea and emesis. Even low level of long term exposure leads to probable kidney problems, respiratory diseases and weak bones. Cadmium, lead and nickel compounds are known toxic metals and disturb the metabolic activity of humans.

Accurate determination of heavy metals estimation has considerable importance in the field of analytical chemistry (Saracoglu, S, 2012)

1.4.3. Toxicity of Chromium (VI)

Compounds of chromium (VI) are known for their toxicity and carcinogenicity. Inhalation of high levels of chromium can irritate nose lining leading to runny nose, ulcers and various breathing problems i.e. flu, cough, short breath and asthma and shortness of breath. Adverse health effects on the liver, intestine, kidney and immune system are related with exposure to chromium (Saha et al, 2011).

1.4.4. Toxicity of Nickel

The earth's crust contains nickel, a metallic element, naturally.

Metallic nickel as well as its compounds have special physical and chemical characteristics that make them useful in modern industry. The main ways that humans are exposed to nickel are through inhaling and ingesting. Through diet and work-related exposure, significant quantities of nickel in various forms may accumulate in the body of an individual over their lifetime.

Because nickel hasn't been identified as a human essential element, it is unclear in what way nickel and its compounds are metabolised (Denkhaus, E., & Salnikow, K., 2002).

Nickel is used in toys because it resists corrosion and has a high conductivity to electricity specifically used in model toys i.e., railway or battery related. (Use of nickel allowed in toys, 2014)

According to International Agency for Research on Cancer (IARC), some nickel compounds are known to cause cancer in humans, and metallic nickel may also do so (TOXICOLOGICAL PROFILE FOR NICKEL).

1.4.5. Toxicity of Copper

Human bones, joints, and ligaments are made up of tissues that copper helps in formation. Diet can provide with a lot of copper. The recommended acceptable and safe intake of dietary copper is 1.5–3.0 mg/day for adults, 0.7–2.5 mg/day for kids and teenagers, and 0.4–0.7 mg/day for newborns (U.S. AF, 1990).

A blood copper level of higher than 140 mcg/dL is considered toxic. The distribution of copper throughout the different tissues depends on factors like age, sex, dietary copper intake, and overall health. When compared to adults, newborns have a liver with 6–10 times more copper (U.S. EPA, 1987). Patients with Wilson's disease, a genetic condition marked by a defective copper metabolism, as well as those with cirrhosis, have high copper levels in their brain, bones, liver and kidneys (Stokinger, 1981; Scheinberg, 1983). Menke's syndrome i.e. kinky hair disease, a neurodegenerative illness, causes low tissue contents of copper as a result of unusually low copper absorption (Aaseth and Norseth, 1986).

The ingested RfD of 0.04 mg/kg body weight/day, which the EPA obtained on the basis of Drinkable Water Standard Levels, is best supported by a thorough evaluation of the research literature. This figure is based on short-term gastrointestinal symptoms, but it is also supported by a more comprehensive examination of copper toxicity and deficiency (Taylor, et al., 2022).

1.5 Human health Risk Assessment of Heavy Metals

The risk assessment is a multi-step process that includes (1) data collection (collecting and analysing site data related to human health), (2) exposure assessment (estimation of the magnitude of actual and/or possible human exposures), (3) toxicity assessment (determination of adverse health consequences associated with exposure to different chemicals), and (4) risk categorization (Gržetić, I., Ghariani, & A.R.H., 2008)

Heavy metals from products can be released in different cases which includes ingestion, inhalation, contact with skin and oral exposure (Guney, 2012). Children behave differently at different life stages while playing with toys i.e. their pathway of exposure to toys vary. After being born to the age of approximately six years, most of the exposure to heavy metals is due to their licking, chewing and mouthing of toys (Kumar, 2007, Tangahu, 2011). This exposure is due to leaching of heavy metals from the surface of toys (Ahmad, N., 2014). Most crucial scenario occurs when children ingest very small fragments of broken toys or painted coating or as a whole.

In this case, the consumed object gets exposure of gastrointestinal tract or makes contact with the saliva in mouth. Low level of pH with raised temperature and internal salts and enzymes for digestion in the stomach and saliva enhances the solubility of toxic metals in the digestive tract.

Almost 50% lead absorbed by gastrointestinal tract is available biologically (Kim, S., 2012,)

Bio accessibility of metal from a certain item can be estimated through in vitro and in vivo assessing procedures. Testing via in vivo methods involves experimentation on living bodies: hence, it has limitations due to ethics and extremely high expense. So, preference is given to in vitro i.e., experiments in labs are preferred.

Due to unavailability of National quality control standards limits for toys in Pakistan or absence of authority for providing toys quality guidelines to ensure safety of children, obtained results will be compared with the regulations provided by other countries of the world i.e. United States Consumer Product Safety Commission (U.S.CPSC) toy safety F963-11, European Union (EU) Toy Safety Directive (European Council 2009), Canadian limits (Government of Canada,2016-2018), and Bureau of Indian Standards (BIS) IS:9873 permissible limits. Hence absence of any published research on bio accessibility of heavy metals in children toys in Pakistan coupled with no national safety standard limits set for toys in Pakistan has necessitated this research project.

1.6. Research Questions

- How to estimate and assess health risk of selected heavy metals in children toys?

The prime research question will be answered, followed by a set of following sub questions:

- How to evaluate total metals concentrations (Pb, Cd, Cr, Cu and Ni) in low-priced children toys available in Lahore local markets? Compare results with

European Union, United States, Canada, and Bureau of India's Toy safety Regulations.

- Characterize health risk assessment based on AAS analysis of total metal concentration and questionnaire responses.

This thesis has been divided into following chapters. Chapter 1 introduces the topic; Chapter 2 gives a detailed literature review regarding health effects of elevated heavy metals in various consumer products. Chapter 3 explains the methodology of thesis; Chapter 4 analyzes the results followed by the findings of the study.

Chapter 2

LITERATURE REVIEW

Hazardous contamination of chemicals or metals in the toys and accessories of children is a common problem everywhere. Addition of metals in order to provide stability, color brightness, softness and flexibility to manufacture the final product which makes it aesthetically attractive to children (Negev, Berman et al. 2018). A large number of studies has been undertaken on the estimation of concentration, distribution, and impacts of heavy metals in various products because of their toxicity. This section covers the study, articles published in various journals of environmental chemistry, ecotoxicology, ecology and analytical chemistry. A brief review of the literature is given as follows:

Lead (Pb) is an unessential heavy metal. Lead exposure has been linked to harmful health outcomes in both kids and adults. Children may be exposed to lead through paint used on toys or other children's products, although this exposure can be avoided. By using cluster sampling, 24 stores in Bogota, capital of Colombia were chosen to take part in the study.

The findings imply that there may be a potential risk of exposure to lead from toys sold in Bogotá's official market. Therefore, it is vitally necessary to create a nationwide strategy for monitoring the presence of lead in children's products. This study's risk of lead exposure in children, which is entirely avoidable, may also exist in other developing nations. (Mateus-García, A., Ramos-Bonilla, & J. P., 2014)

Researchers (Greenway, J. A., and Gerstenberger, S., 2010) evaluated lead toxicity in the day care center children’s plastic toys in Las Vegas, United States of America. Data suggested that lead usage as stabilizer of polyvinyl chloride (PVC) plastic products elevated the lead concentration i.e. 600 ppm when compared with non PVC products. Yellow colored toys consist of elevated concentration of lead than other toys due to use of lead chromate as coloring pigment. Twenty nine out of five hundred and thirty five toys contained lead more than 600pm. 20 toys were PVC out of 29 toys.

On the other hand, Abhay Kumar and Prashant Pastore conducted a study in India in which they determined total cadmium and lead concentration in soft plastic. The present study was undertaken to ascertain the levels of total lead and cadmium in soft toys. 111 samples of toys with no renowned brand were collected from metropolitan cities of India randomly (Delhi, Chennai and Mumbai). Lead and cadmium were detected in all the samples in different concentrations. It is most widely accepted that any amount of cadmium (Cd) or lead (Pb) in blood should be unsafe for individuals especially children. Therefore, every possible attempt should be made to ensure toxic constituent free environment for them. PVC in toys has probability to cause toxicity in children due to presence of Cd and Pb. Main route of exposure of these metals is through mouth i.e. biting and swallowing (Abhay Kumar and Prashant Pastore 2007).

Moreover, a group of scientists in China examined the routes of exposure of cadmium, lead, barium, chromium and mercury and their health impacts on children. Routes of exposure included oral consumption, skin absorption, and inhalation as a result of heavy metals contact with human beings. Health implications to children were more serious than adults a ..1s a result of heavy metal consumption. These elements' hazardous health implications on children include mental disability, damage to neurocognitive functions of brain, behavioral disability, breathing problems, heart diseases and cancer. Hence, heavy metals exposure to children should be given considerable attention because they have definite potential due to spread toxicity, prevalence and common usage in daily life (Muwaffak Al osman, Fei Yang, & Isaac Yaw Massey, 2019).

This review's attention was drawn to the toxicity of heavy metals and how it is estimated using various analytical methods that are currently under research. Heavy metals are present in a variety of consumable and non-consumable products which can be used as carriers for active chemicals or catalysts as well as to produce a range of impacts, such as toxicity. Ayurveda claims that these heavy metals have been changed into nontoxic forms that are acceptable for internal use, ignoring the fact that different analytical techniques used to do current chemical analyses on these results clearly demonstrate the presence of heavy metals, which is not safe (kumar Das, S., singh Grewal, A., & Banerjee, M., 2011).

A quantitative and socioeconomic analysis of selected heavy metals (arsenic, lead and cadmium) in toy accessories and jewelry of children was performed by five researchers in United States. Quantitative analysis was performed with multiple techniques. Outcome of the research suggested that purchase marketplace was a prominent factor comparing to the cost of the product. Fifty seven percent of the toy products were from bargained stores were compared to fifteen percent of retail market cheap items. Jewelry toys were the most hazardous products including seventy three percent of the bargained non-compliant toys. Arsenic and lead were the most common toxic compounds in the samples of non-compliant toys. They highlighted a socioeconomic public issue regarding health using Richmond area as a model, cheap and least income bargain marketplaces increasing in number (M. Hillyer, 2014).

Likewise, contamination of 11 hazardous elements was assessed in the toys and jewelleries of children from the Asian shops of Kazakhstan. Analysis in laboratory showed that most of the samples had heavy metals more than permissible limits mentioned in the United States, European Union and Canadian standards or legislation. Due to toxicity and health risk of these elements, recommendation was given to assess the bioavailability of these metals in human beings. The results were evidence for widespread issue of heavy metal contamination in children accessories and toys of underdeveloped countries (Akimzhanova, Z., Guney, M., Kismelyeva, S., Zhakiyenova, A., and Yagofarova, A., 2020)

A feature in United States in 2010 was reviewing the current situation of toxic substances in children accessories and making recommendation to government and manufacturers for future. Toxic substances in the goods used by consumers is a widespread problem and a matter of concern. Since children have less mass on their body, they are most sensitive to hazardous chemicals in their toys. Exceeding concentration of lead (Pb) and cadmium (Cd) in the products of children and plastic components including bisphenol and phthalates are harmful for health. Introduction of REACH by Europe and review of TSCA by United States are a step in the right direction. But increasing products globally pose question and concern for management of supply chain and legal reach (Becker, M. E.,2010)

However, a CDC report of death due to lead toxicity was reported in Minnesota. The reason reported was the ingestion of metal charm consisting of lead. The charm was attached with metallic bracelet gifted by a shoe company. Paint coatings consisting of lead has been common exposure of lead for children less than six years of age. In this case, proper testing was performed by digesting the ingested metallic charm in acid by Minnesota Laboratory department following protocols of EPA concluded high concentration of lead. Prohibition of lead based paint in the items used by consumers should be an essential proactive approach by every manufacturer (CDC, 2006).

Similarly, a case was reported by disease control and prevention center of US (CDC) in which a toy resembling necklace was ingested by a child and it lead to poisoning. Lead poisoning used to be one of the main source of after effects of exposure to paint coatings consisting of lead. Such ingestion of products leads to increased level of lead in blood (CDC, 2003).

Despite the restrictions imposed by organizations like the WHO standard, the toy's paint contains a significant amount of heavy metal, which would be a cumulative harmful source. Three various colors of plastic toys—black, red, and yellow—that are appropriate for children between the ages of three and six years old were gathered. The SPSS software study reveals a high correlation between heavy metal content and various parameters, with the exception of the correlations between lead and pricing and nickel and color, in which the black color toys had a high proportion of heavy metal (Al Kindi, G., Y., Ali, & Z. H., 2020)

A study was conducted on health risk assessment of children accessories i.e. toys and jewellery; coupling factor of bio accessibility of such metals. Contamination of such metals in children toys was determined. It was concluded that amount of lead, chromium, cadmium and nickel in jeweled toys exceeded the safety limits of European Union. Assessment of hazard index of jewelry of toys was based on saliva movement and ingestion by mouth. Hazard index was impermissible for cadmium, chromium, arsenic and antimony. Hence data from this study propels attention towards importance of bioavailability of such metals from toys and jewelry of children (Cui X, 2015)

In order to determine the toxicity of the heavy metals used in play paints, a study was carried out in Portugal. Play paints for kids may include heavy metals due to their pervasiveness and durability. Numerous product types, colors, brands, and countries of manufacture were examined to detect the presence of Pb, Cd, Cr, Co, Ni, Mn, and Zn. A safety evaluation was conducted, taking into account the projected possible exposure and health-based limitations (tolerable daily intakes). Overall, the findings did not point to any causes for concern about the tested elements' safety (Rebelo, et al., 2015)

By using X-ray fluorescence spectrometry, 200 used plastic toys from the UK were examined for toxic elements (As, Ba, Cd, Cr, Hg, Pb, Sb, Se), as well as Br, a stand-in for fire retardants.Recent EU consumer product safety directive stipulated migration limits for Cd and Pb respectively. In eight cases, Cd emitted via yellow and red Lego bricks surpassed its limit by an order of magnitude.

On the basis of migratable Cr, two further examples were probably noncompliant, and one of the items additionally included >250g migratable Br. Old, mouthable, plastic goods may present a source of infants exposure to hazardous elements, despite the fact that there is no retroactive regulation on used toys (Turner, A., 2018).

Andrew Turner examined the prevalence and accessibility of cadmium in consumer goods. In trace amounts, recycled plastics contain cadmium. The measurements of Cd in historical and modern products determined by XRF are given, with an emphasis on bright-colored cadmium sulphide and sulphoselenide pigmentations. Cadmium is present in a wide variety of modern plastic items, primarily due to the unregulated recycling of polyvinyl chloride and electronic trash. The usage of cadmium pigments in the enamels of decorative drinking glasses has been identified as the biggest consumer danger. Although they don't seem to pose a direct threat to health, glass bottles adorned with cadmium-based enamel have a tendency to contaminate recyclable glass items. Better regulations for decorative glassware are advised, as well as caution while handling used, vividly colored toys (Turner, A, 2019)

By using extraction methods that simulate oral exposure of jewelry ornaments, researchers in United States assessed the bioavailability of cadmium that were reported to have elevated levels of cadmium. They used X - ray diffractometer to determine cadmium concentration. There were two approaches to measure bioavailability. Leaching of cadmium in diluted Hydrochloric acid suggested that the potential for harm may rise in the stomach.

Cadmium release was often, but not always, increased when jewelery was damaged by breaking through the exterior plating. There was no direct relationship between bioavailability and Cd content. These findings suggest that children who wear, ingest, or unintentionally swallow high-Cd jewellery items may be exposed to harmful levels of Cd (Weidenhamer, J. D., Miller, J., Guinn, D, & Pearson, J. , 2011).

For purposes of health and safety, quality control of toys is a typical requirement in national and/or international rules. This is important because it prevents children from being exposed to potentially hazardous materials. For the direct examination of plastic toys, laser-induced breakdown spectroscopy was recently tested at the one of the Brazilian laboratory. Classification models were created from the emission spectra of polymeric toys. The classification techniques and data validation were performed. The KNN method produced the best results, with corrected predictions ranging from 95% accuracy for Cd to 100% accuracy for Cr and Pb.

Some samples of play dough, face paint, and finger paint in Turkey contain heavy metals. A novel technique solid multiwalled carbon nanotubes was used to evaluate them. Evaluation of the outcomes was compared with EU regulations. Zeliha, Mustafa and Aslihan in 2011 looked at analytical characteristics such pH, ligand concentration, and sample solution volume that could influence the performance of formation of complexes and solid phase extraction. The findings of this study demonstrated the danger that such toys pose to young children. The findings of this investigation indicated that samples of toys include heavy metals in various quantities. As a result, research's findings indicated that these types of toys put kids' health at danger. (Godoi, et al., 2011)

In half of the total childcare goods, including children's jewelry pieces, toys, nappy mats, baby sleepers, baby fabrics, and feeding and bathing items, scientists tested for regulated and unregulated pollutants. Such items could have high oral or skin exposure. In Israel, jewelry for kids is an unregulated good. 23 percent of children's jewel accessories surpassed US lead standards. Up to 45% of particular baby goods had phthalates and BPA levels over EU limits. Products that are regulated typically meet requirements, whereas unauthorized products are contaminated. (Negev, et al., 2018)

To determine the presence or absence of risks that these heavy metals pose to children, the availability and concentration of potentially hazardous metals in toys for kids were measured. The samples of 25 imported toys via China to Nigeria had been collected. The amounts of toxic metals that might leak out from the toys during children's mouthing behavior patterns, such as chewing, sucking, and swallowing, were calculated using ternary acid digestion, Atomic Absorption Spectrophotometry, and simulations of the saliva and gastric juice extraction conditions.

The overall toxic metal concentration and toys made of PVC materials had a positive association, according to statistical analysis. The risk evaluation study revealed hazard index of 4.50 for saliva extraction which suggests that Cd posed the greatest risk. More vigilance was needed, according to the study (Oyeyiola, A. O., 2017).

The purpose of research conducted in Karachi last year was only to evaluate the total metal content of copper, lead, chromium zinc, nickel and manganese in plastic toys for children but they did not held health risk assessment based on US EPA model.

To safeguard the safety of Pakistani children, there are no norms or quality control authority rules, notably for toys. As a result, the obtained findings were contrasted with those of other rules that were accessible in various nations and places. Lead and Cadmium are both metals that are the prime focus of current research because both are recognized as carcinogens, cytotoxic agents, and nephrotoxins. The findings showed that the children's toys sold in Karachi's local marketplaces have high concentrations of nickel, chromium, lead and cadmium with low concentrations of manganese, zinc and copper. (Gul, et al., 2022).

Hence, this is Pakistan's first scientific analysis that assesses health risk and socioeconomic considerations of plastic toys for kids.

Chapter 3

METHODOLOGY

This chapter entails the methodology adopted to achieve the objective of this study that is, the estimation of heavy metals in various children toys and their resulting health risks. Whole study was divided into following parts:

- Desk study
- Collection of toy samples
- Estimation of heavy metals
- Questionnaire based survey

3.1 Desk Study

Desk study involved two parts:

- Review of previous research work
- Questionnaire formation and analysis

3.2 Review of Previous Research Work

Various studies had been undertaken on the estimation of concentration, distribution, and impacts of heavy metals in various children toys. Some of the toy samples were subjected to wet digestion in a combination of nitric acid, sulphuric acid, and hydrogen peroxide, and others were subjected to the dry ashing method.

A lot of studies did health risk assessment but there is no such research done in Pakistan yet. Some researches revealed that number of heavy metals were higher than World Health Organization’s permissible values. Few studies considered that concentrations less than permissible limits still posed problems since their consistent usage leads to hazardous effects on human health. This is due to bioaccumulation.

3.3 Questionnaire Formation and Analysis

The objective of this research was to determine whether toys bought by people with low and average incomes pose a health risk factor and to establish standards and laws to regulate the trade in children's toys. 50 copies of developed questionnaire were used to evaluate the socioeconomic circumstances of the household, including occupation, education, and income, as well as the type and caliber of the kids' toys, awareness of the health risks associated with particular toys, and the prevalence of specific associated health issues. Completed questionnaire copies are represented in results.

It was designed during our desk work by going through research papers and utilizing information given by the study (Korfali, S. I., Sabra, R, Jurdi, M., & Taleb, R. I. , 2013) and hence, questionnaire was put together. The responses are given in chapter 4.

3.4 Sample Collection

A total of twenty plastic toys for children under the age of five were sourced from various local shops in Lahore, Pakistan. The area of the samples collected is shown in Figure 1. Toy samples were selected at random from local shops, stalls, mall shops, discount shops, outdoor vendors, and retail stores.

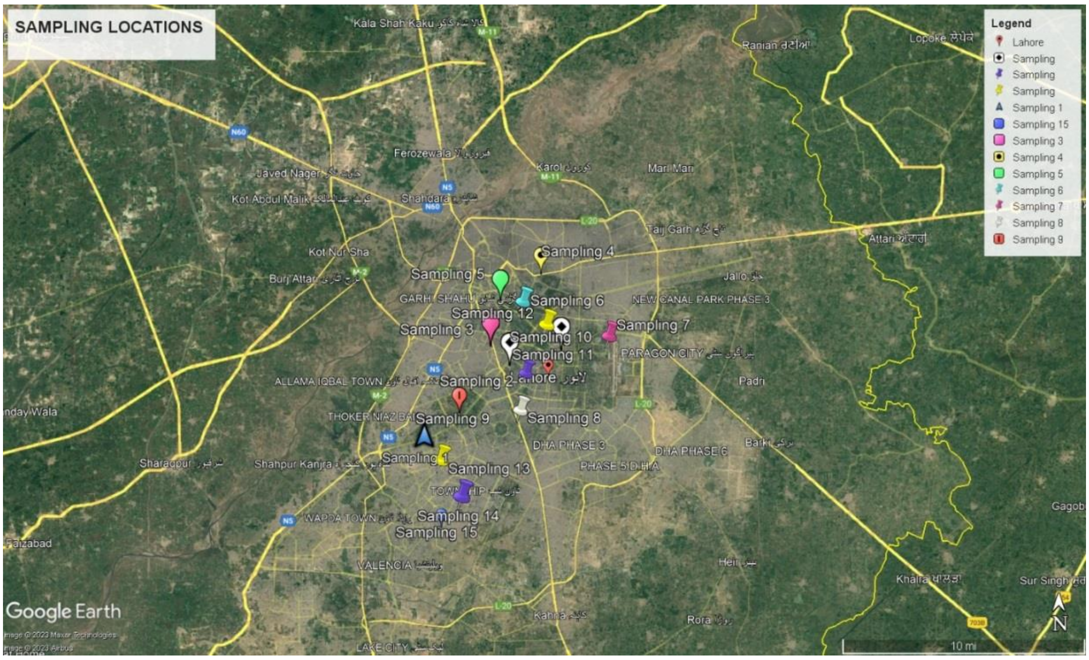


Figure 3.1 Location of samples collected from various local shops in Lahore, Pakistan.

The samples were chosen based on the potential for mouthing by young children under the age of 5, choosing those inexpensive plastic toys that were primarily desired by low-income groups and created for young children. Low-cost samples were given preference during the selection process. This was due to earlier studies that claimed that less expensive toys may contain higher quantities of metals due mostly to the recycling of contaminated materials or the absence of raw materials regulation (Kang and Zhu, 2013; Weidenhamer and Clement, 2007a,b).

The plastic toys featured rattles, playdough or clay, teethers, baby's hard car toys, soft animal and fruit toys. The majority of the selected toys and clays had "Made in China" labels, and rest of the toys had local production plants.

Cadmium (Cd), Chromium (Cr), Lead (Pb), Copper (Cu) and Nickel (Ni) were examined for their potential health risks in terms of total metal content.

Table 3.1: Samples labelled with sample codes.

Sr.	Sample Labels	Samples
1	Sample A	Teethers
2	Sample B	Rattles
3	Sample C	Cars
4	Sample D	Clay/ Play dough
5	Sample E	Robot characters
6	Sample F	Cartoon characters
7	Sample G	Animal characters
8	Sample H	Soft plastic fruits
9	Sample I	Dark colored Ship
10	Sample J	Light colored ship
11	Sample K	Bright colored stars shapes
12	Sample L	Light colored star shapes
13	Sample M	Bright colored yellow balls
14	Sample N	Multicolored soccer balls
15	Sample O	Orange bath football toy
16	Sample P	Alphabetic toys
17	Sample Q	Numeric representation musical toys
18	Sample R	Colored blocks
19	Sample S	Kitchen set
20	Sample T	Ringing shape toys

3.5 Determination of total Metal Concentration [Ni, Cu, Cd, Pb, and Cr (VI)] in Toy Samples

3.5.1. Preparation of Samples

With scissors and cutters, plastic toys were broken up into tiny pieces (0.5 cm ×0.5 cm), and paint coating samples and brittle/pliable toys were ground into powder.

For the purpose of measuring concentration, an aliquot of 0.5 g of sample was utilized for each component. Small pieces of hard plastic toy samples that would come into touch with children were sampled for measurement after being disassembled.

Fig 3.2. Prepared samples after crushing into small pieces of size of 0.5 cm.

3.5.2, Digestion and Dilution of Samples

In porcelain crucibles, 0.5g of each sample was weighed, and then by adding 10 ml of analar graded concentrated hydrochloric acid, nitric acid, and per chloric acid each sample was heated until fuming stopped. The mixture was diluted to the proper volume in a 50 ml volumetric flask. Following that, it was filtered through Whatman filter paper. After that, samples were examined using flame atomic absorption spectroscopy for the presence of Ni, Cu, Cd, Pb, and Cr (VI) (FAAS).

(a)

(b)

Fig 3.3. Samples during digestion and dilution

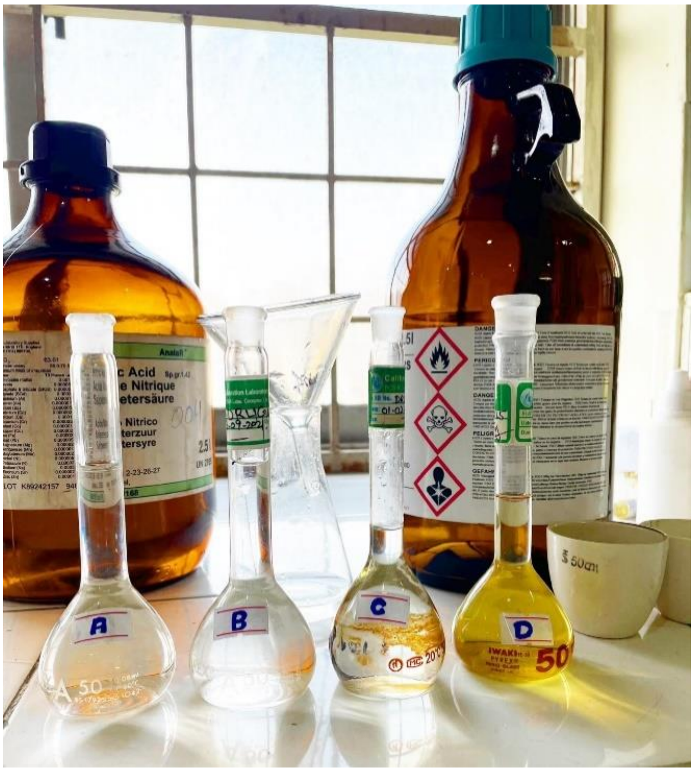


Fig 3.4. Samples after dilution

3.5.3. Detection of Total Heavy Metal Concentration in AAS

Concentration of cadmium, chromium (VI), nickel, lead and copper were subjected to detection. First, the standards of samples were prepared and then analyzed in Atomic absorption spectrophotometer.

Fig 3.5. Samples detection on atomic absorption

3.5.3.1. Standards Preparation

Standards solutions for metals were prepared for following concentrations 2ppm, 4ppm and 6ppm. For cadmium standards of 5 ppm, 10 ppm and 15 ppm were prepared. For instance, stock solution of 1000ppm were taken to prepare 100 ppm solution out of which 2, 4 and 6 ppm samples were prepared as: 2ml sample taken from 100 ppm solution and 98ml of distilled water is added. This is done by following formula:

$$C1V1 = C2V2$$

3.5.3.2: Analysis of Samples

First of all, blank solution was run to calibrate the instrument. Twenty samples of plastic toys labelled A, B, C, and D were run after preparing standards and calibrating the instrument for the detection of copper, cadmium and chromium.

These methodologies were done in prior studies (Oyeyiola, 2017, Terry Mohammed, et al., 2020). The sample preparation and analysis of samples were conducted at Pakistan Council of Scientific & Industrial Research (PCSIR) in Lahore.

Fig 3.6: Blank solution run to calibrate the instrument

3.6. Permissible limit of heavy metal concentration

Regulations set by Indian Bureau for Toy Safety (BIS), Canadian, United States and EU Directive were compared with the results of samples induced by AAS.

Heavy metals	**EU Regulation**		
	Dry, powder, brittle stuff	Sticky & liquidy stuff	Scrapped toy stuff
Cd	1.3	0.3	17
Cr	37.5	9.4	460
Pb	2	0.5	23
Cu	622.5	156	7700
Ni	75	18.8	930

Table 3.2: Permissible limit of heavy metal concentration set by European Union (EC 2009), the United States (US CPSC) (ASTM International 2017), Canada (Gov. of Canada 2011, 2018), and BIS (Bureau of Indian Standard).

Heavy metals	**Canada Regulations**		
	Consumer products	**Jewelry**	**Coatings for toy surface**
Cd	130	-	1000
Cr	-	-	-
Pb	90	90	90
Cu	-	-	-
Ni	-	-	-

Table 3.3: Permissible limit of heavy metal concentration set by Canada (Gov. of Canada 2011, 2018).

Heavy metals	US limits			BIS
	Children products	Soluble clay for modeling	Toy's Coating & substrates	
Cd	200 μg	50	75	75
Cr	-	25	60	60
Pb	100	90	90	90
Cu		-	-	-
Ni	-	-	-	-

Table 3.4: Permissible limit of heavy metal concentration set by United States (US CPSC) (ASTM International 2017) and BIS (Bureau of Indian Standard).

3.7. Health Risk Assessment Study

The USEPA was used to adapt the health assessment for carcinogenic and non-carcinogenic risks (2009). Nickel, Chromium Cr (VI), and lead are proven carcinogens, whereas copper is known to be non-carcinogen in human beings (The Risk Assessment Information System., 2007).

The United States developed models for assessing health risk (U.S EPA, 1991). These models have been fully developed, are accessible through the information system of risk assessment (RAIS), and are backed by toxicological profiles created and acquired by Integrated Risk Information Management System of USEPA. The US Agency for Registry of Toxic Substances and Diseases also supports it (ATSDR).

3.8 Non-Carcinogenic Dose Response Assessment

This assessment is carried out in order to calculate the dose of a toxic substance exposed to a person and the possible health effects in response to that dose. The dose could be exposed through three types of routes i.e. absorption through skin, ingestion through mouth and inhalation from mouth and nostrils.

In case of heavy metals present in children toys, the dose is exposed through ingestion because newborns, toddlers, and young children frequently mouth toys. Here risk assessment is carried out using the method described in a previous research (Terry Mohammed, et al., 2020).

The average daily dose of ingestion (ADD) was used to assess the non-carcinogenic health risk (Ismail et al., 2017):

$$ADD = \frac{C_{sample} \times IR \times EF \times ED}{BW \times AT} \qquad \text{(Equation 1)}$$

Here,

ADD = Average Daily Dose of Ingestion (mg/kg/day)

C_{sample}= Heavy metal Concentration in sample (mg/kg)

IR = Intake/Ingestion Rate (kg/day)

EF = Exposure Frequency (days/year)

ED = Exposure Duration (year)

BW = Body Weight (kg)

AT = Averaging Time (period over which exposure is averaged) (days)

$$HQ = \frac{ADD}{RfD} \qquad \text{(Equation 2)}$$

Heavy metal Concentration in sample were determined in PCSIR in this study, while other factors were set to the default value found in (Grẑetic I. & Ghariani R. H. A., 2008) . The default value for each parameter in the health risk calculation is described in **Table 3.5**. below.

Hazard Quotient was determined by using ratio of absorbed daily dose to the Reference Dose (Eq. 2). RfD is an estimation of a repeated exposure on daily basis to the humans, which includes sensitive subgroups, that is expected to not pose a significant lifetime risk of adverse consequences. The RfD is typically stated in milligrams (mg/kg/day) per kilogramme of body weight each day. RfD used to evaluate point of reference to determine the chemical's possible effects at various concentrations. Usually, dosages below the value of RfD are not considered to have harmful effects.

While doses above the RfD are probably linked to negative health consequences, which is concerning,

Table-3.5. Input Parameters for Average Daily Dose

Variables in formula used	Values
Ingestion rate (IR) of a kid	0.0002 kg/day (Grẑetic I. & Ghariani R. H. A., 2008)
Exposure frequency (EF)	365 days/ year (USEPA, 2009)
Exposure duration (ED) for non-carcinogenic metals	6 years (Grẑetic I. & Ghariani R. H. A., 2008)
Exposure duration (ED) for non-carcinogenic metals	70 years (USEPA, 2009)
Body weight (BW)	15 kg (Grẑetic I. & Ghariani R. H. A., 2008)
For non-carcinogens: AT (Averaging Time)	Actual ED * 365 days per year and intake is called Chronic Daily Intake = 2190 days
For carcinogens: AT (Averaging Time)	Lifetime (70 years) * 365 days per year and intake is called Lifetime Average Daily Dose (LADD)= 25550 days

Table 3.6: Reference Dose (RfD) for oral consumption associated with non-carcinogenic risks.

Heavy Metals	**RfD** (mg/kg-d)
Cd	0.001 (US EPA, 2010)
Cr (VI)	0.003 (IRIS, 2008)
Pb	0.0035 (WHO, 1993)
Cu	0.04 (USEPA,2016)
Ni	0.02 (IRIS, 2005)

3.9. Statistical Analysis

The obtained results from Atomic Absorption Spectrophotometer were analyzed. Mean concentrations and standard deviations of all samples were obtained and represented through bar charts in Origin Software. This tool was used to get help to easily identify the highest and lowest concentrations of heavy metals in different samples.

Chapter 4

RESULTS AND DISCUSSION

4.1. Results

This chapter aims for the outcomes of amount of heavy metals in children toys. The total number of samples were twenty which were analyzed for five heavy metals (Lead, Cadmium, Chromium, Copper and Nickel). This chapter comprises of three parts:

(Part 1) includes the results of all metals' mean concentrations were analyzed by atomic absorption spectrophotometer.

(Part 2) includes Exposure Evaluation by filling Questionnaire responses.

(Part 3) of the study involved dose response assessment.

(First part of study)

4.1.1.1. Cadmium

Cadmium is a metal used to brighten color schemes and to provide stability to plastic, similar to lead, to stop the creation of hydrochloric acid that would otherwise causes the polymer to deteriorate (Kumar and Pastore, 2007).

It has been determined that cadmium (Cd) is a type I carcinogenic heavy metal. Cd is probably closely associated to oral cancers because it is taken orally via food and smoking and alcohol use. (Samed Satir, 2022)

Cadmium concentration was found in most of the samples observed. Sample I (Dark colored ships) had the highest concentration (81 mg/kg) of cadmium and almost negligible concentration was detected in sample A (teethers), sample L (star shaped pacifiers) and sample M (green and yellow balls) as shown in table below:

Table 4.1. Concentration of Cadmium in 20 samples

Sr.	SAMPLE LABELS	SAMPLES	CADMIUM CONCENTRATION (mg/kg)
1	Sample A	Teethers	0.07
2	Sample B	Rattles	N/A
3	Sample C	Cars	83.7
4	Sample D	Clay/ Play dough	0.14
5	Sample E	Robot characters	68
6	Sample F	Cartoon characters	16.1
7	Sample G	Animal characters	78.2
8	Sample H	Plastic fruits	16
9	Sample I	Dark colored Ship	81
10	Sample J	Light colored ship	75.5
11	Sample K	Pacifier stars shaped (bright)	0.3
12	Sample L	Pacifier star shaped (grey)	N/A
13	Sample M	Green and yellow balls	N/A
14	Sample N	Pink and blue soccer balls	45.1
15	Sample O	Doctor Toy Set	32.2
16	Sample P	Alphabetic toys	0.017
17	Sample Q	Numeric representation musical toys	0.031

18	Sample R	Colored blocks	0.22
19	Sample S	Kitchen set	24.5
20	Sample T	Ringing shape toys	0.81

Average concentration: 26.08945

Maximum concentration: 83.7

Minimum concentration: N/A

Samples exceeding EU limit: 40% (8)

Samples exceeding US limit: 25% (5)

Samples exceeding Canadian regulation: -

Samples exceeding BIS regulations: 25% (5)

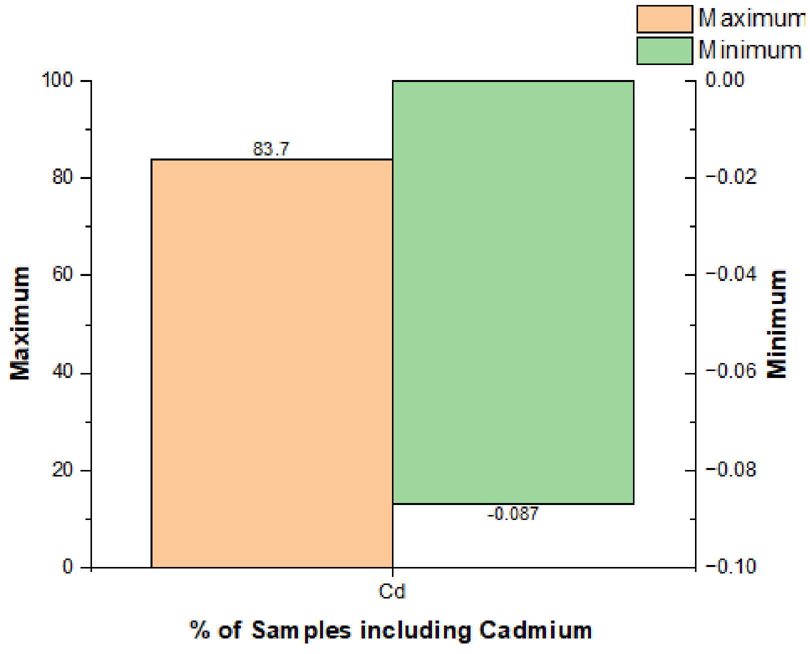


Fig 4.1. Percentage, maximum and minimum concentration of samples including cadmium

4.1.1.2. Chromium (VI)

Oral exposure is not known to be carcinogenic, so it is categorized in Group D. It is impossible to determine whether Cr (VI) causes oral cancer. There was no evidence in the existing literature that Cr (VI) is cancerous when exposed orally. By way of inhalation, Cr (VI) is categorized as a Group A known carcinogen to humans.

Chromium concentration was found in most of the samples observed. Sample E (Robot characters) had the highest concentration (806) mg/kg) of chromium and almost negligible concentration was detected in sample D (clay/ play dough), sample H (Soft plastic fruits), sample J (ship), sample N (pink and blue soccer balls) and Sample T (ringing shape toys) as shown in table below:

Table 4.2: Concentration of Chromium in 20 samples

Sr.	**SAMPLE LABELS**	**SAMPLES**	**Chromium (VI) CONCENTRATION (mg/kg)**
1	Sample A	Teethers	4.5
2	Sample B	Rattles	0.7
3	Sample C	Cars	423
4	Sample D	Clay/ Play dough	N/A
5	Sample E	Robot characters	806
6	Sample F	Cartoon characters	1.5
7	Sample G	Animal characters	231
8	Sample H	Soft plastic fruits	N/A
9	Sample I	Dark colored Ship	102
10	Sample J	Light colored ship	N/A
11	Sample K	Pacifier stars shaped (bright)	0.3
12	Sample L	Pacifier star shaped (grey)	1.5
13	Sample M	Green and yellow balls	271

14	Sample N	Pink and blue soccer balls	N/A
15	Sample O	Doctor Set	0.7
16	Sample P	Alphabetic toys	283
17	Sample Q	Numeric representation musical toys	103
18	Sample R	Colored blocks	1.7
19	Sample S	Kitchen set	2.1
20	Sample T	Ringing shape toys	N/A

Average concentration: 111.59664

Maximum concentration: 806

Minimum concentration: N/A

Samples exceeding EU limit: 5% (1)

Samples exceeding US limit: 35% (7)

Samples exceeding Canadian regulation: -

Samples exceeding BIS regulations: 35% (7)

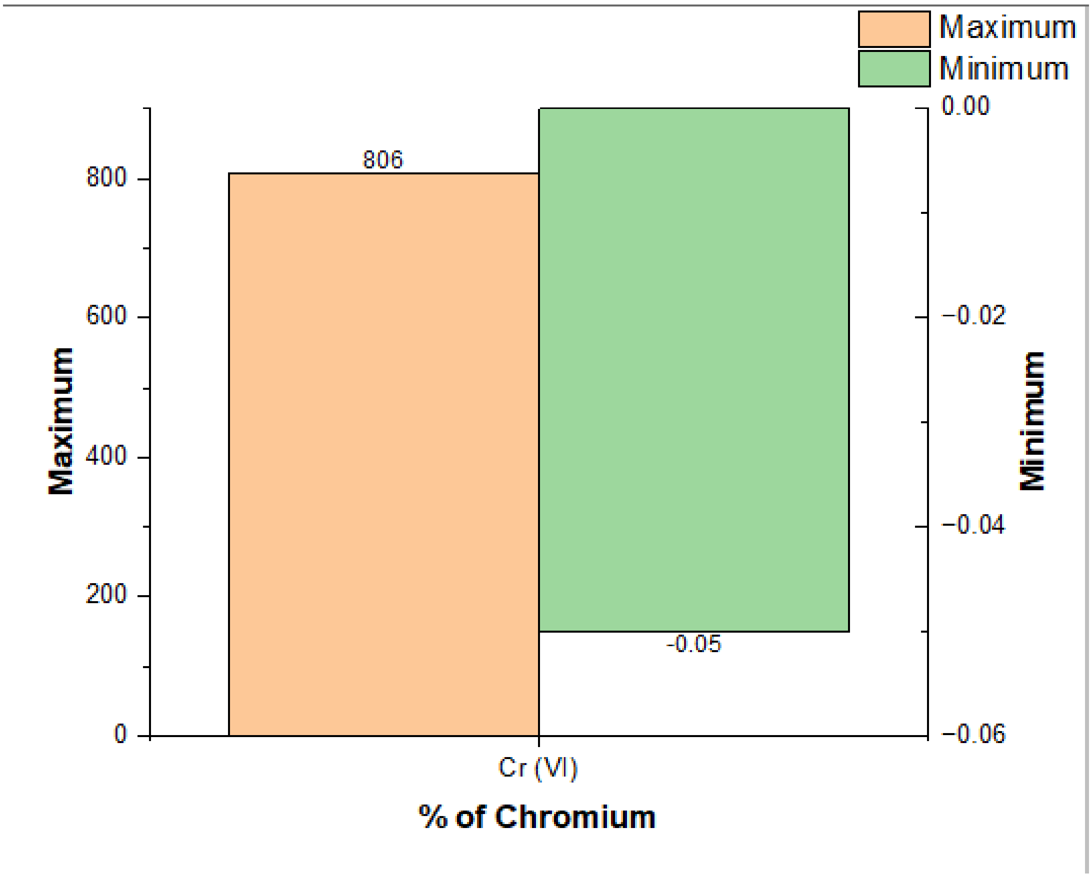


Fig. 4.2. Concentration of Cr (VI) in selected children toys.

4.1.1.3. Lead

Lead concentration was found in most of the samples observed. Sample C (Cars) had the highest concentration (1001 mg/kg) of lead and almost negligible concentration was detected in Sample T (Ringing shape toys) as shown in table below:

Table 4.3: Concentration of Lead in 20 samples.

Sr.	SAMPLE LABELS	SAMPLES	Lead CONCENTRATION (mg/L)
1	Sample A	Teethers	14.7
2	Sample B	Rattles	1.8
3	Sample C	Cars	1001
4	Sample D	Clay/ Play dough	0.8
5	Sample E	Robot characters	411
6	Sample F	Cartoon characters	189

7	Sample G	Animal characters	78.4
8	Sample H	Soft plastic fruits	40.5
9	Sample I	Dark colored Ship	87.7
10	Sample J	Light colored ship	0.5
5.4	Sample K	Pacifier stars shaped (bright)	N/A
12	Sample L	Pacifier star shaped (grey)	0.3
13	Sample M	Green and yellow balls	211
14	Sample N	Pink and blue soccer balls	39.1
15	Sample O	Doctor Set	23.3
16	Sample P	Alphabetic toys	0.24
17	Sample Q	Numeric representation musical toys	0.15
18	Sample R	Colored blocks	75.5
19	Sample S	Kitchen set	83.3
20	Sample T	Ringing shape toys	N/A

Average concentration: 112.9139

Maximum concentration: 1001

Minimum concentration: -0.008

Samples exceeding EU limit: 55% (11)

Samples exceeding US limit: 20% (4)

Samples exceeding Canadian regulation: 20% (4)

Samples exceeding BIS regulations: 20% (4)

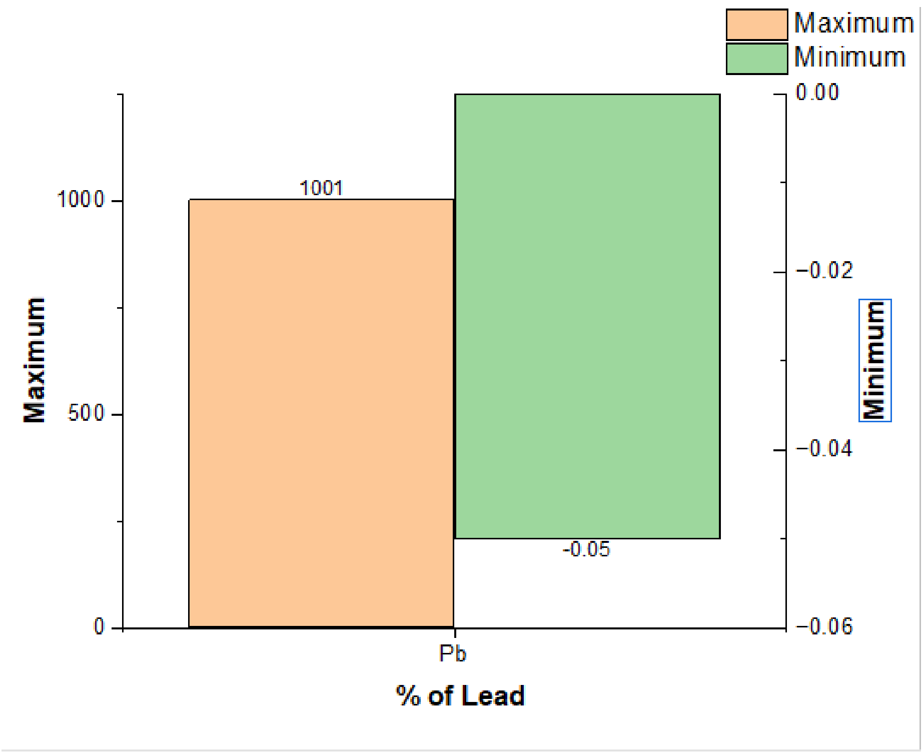


Fig 4.3. Concentration of Lead in selected children's toys.

4.1.1.4. Copper

Copper concentration was found in most of the samples observed. Sample G (Animal characters) had the highest concentration (822 mg/kg) of lead and almost negligible concentration was detected in Sample A (teethers), sample B (rattles) Sample K (pacifier stars shaped bright colored, sample O (doctor set), and sample S (kitchen set) as shown in table below:

Table 4.4: Concentration of Copper in 20 samples

Sr.	**SAMPLE LABELS**	**SAMPLES**	**Copper CONCENTRATION (mg/L)**
1	Sample A	Teethers	N/A
2	Sample B	Rattles	N/A
3	Sample C	Cars	209
4	Sample D	Clay/ Play dough	18.2
5	Sample E	Robot characters	442
6	Sample F	Cartoon characters	309

7	Sample G	Animal characters	822
8	Sample H	Soft plastic fruits	118
9	Sample I	Dark colored Ship	51
10	Sample J	Light colored ship	24
11	Sample K	Pacifier stars shaped (bright)	N/A
12	Sample L	Pacifier star shaped (dark)	1.7
13	Sample M	Green and yellow balls	202
14	Sample N	Pink and blue soccer balls	35.8
15	Sample O	Doctor set	N/A
16	Sample P	Alphabetic toys	429
17	Sample Q	Numeric representation musical toys	326
18	Sample R	Colored blocks	1.4
19	Sample S	Kitchen set	N/A
20	Sample T	Ringing shape toys	254

Average concentration: 162.1484

Maximum concentration: 822

Minimum concentration: N/A

Samples exceeding EU regulations: -

Samples exceeding US regulations: -

Samples exceeding Canadian regulation: -

Samples exceeding BIS regulations: -

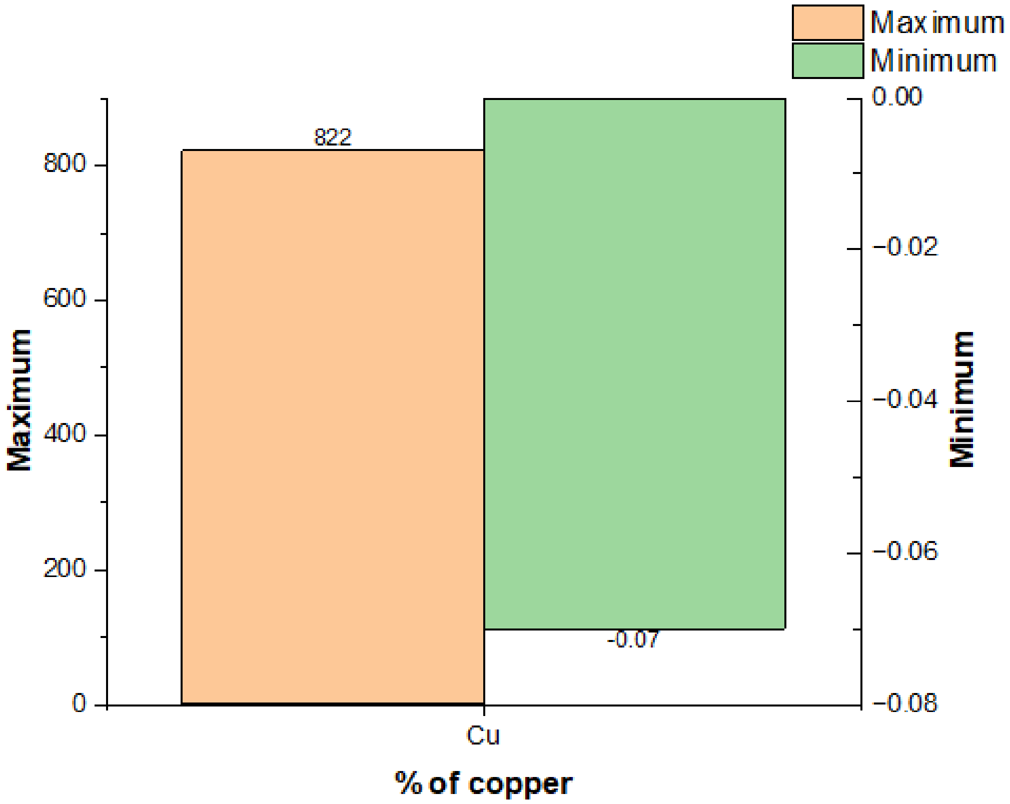


Fig 4.4. Concentration of Cu in selected children's toys.

4.1.1.5. Nickel

Nickel concentration was found in most of the samples observed. Sample E (Robot characters) had the highest concentration (3000 mg/kg) of nickel and almost negligible concentration was detected in Sample A (teethers), sample H (soft plastic fruits), Sample J (light colored ship) and sample N (pink and blue soccer balls) as shown in table below:

Sr.	SAMPLE LABELS	SAMPLES	NICKEL CONCENTRATION (mg/kg)
1	Sample A	Teethers	N/A
2	Sample B	Rattles	4.9
3	Sample C	Cars	380
4	Sample D	Clay/ Play dough	2.9
5	Sample E	Robot characters	3000
6	Sample F	Cartoon characters	160
7	Sample G	Animal characters	225
8	Sample H	Soft plastic fruits	N/A
9	Sample I	Dark colored Ship	390
10	Sample J	Light colored ship	N/A
11	Sample K	Pacifier stars shaped (bright)	4.2
12	Sample L	Pacifier star shaped (grey)	8.3
13	Sample M	Green and yellow balls	318
14	Sample N	Pink and blue soccer balls	N/A
15	Sample O	Doctor set	3.2
16	Sample P	Alphabetic toys	0.80
17	Sample Q	Numeric representation musical toys	0.75
18	Sample R	Colored blocks	2.9

19	Sample S	Kitchen set	6.2
20	Sample T	Ringing shape toys	14.2

Table 4.5: Concentration of Nickel in 20 samples

Average concentration: 259.526

Maximum concentration: 3000

Minimum concentration: N/A

Samples exceeding EU limit: (1) 5%

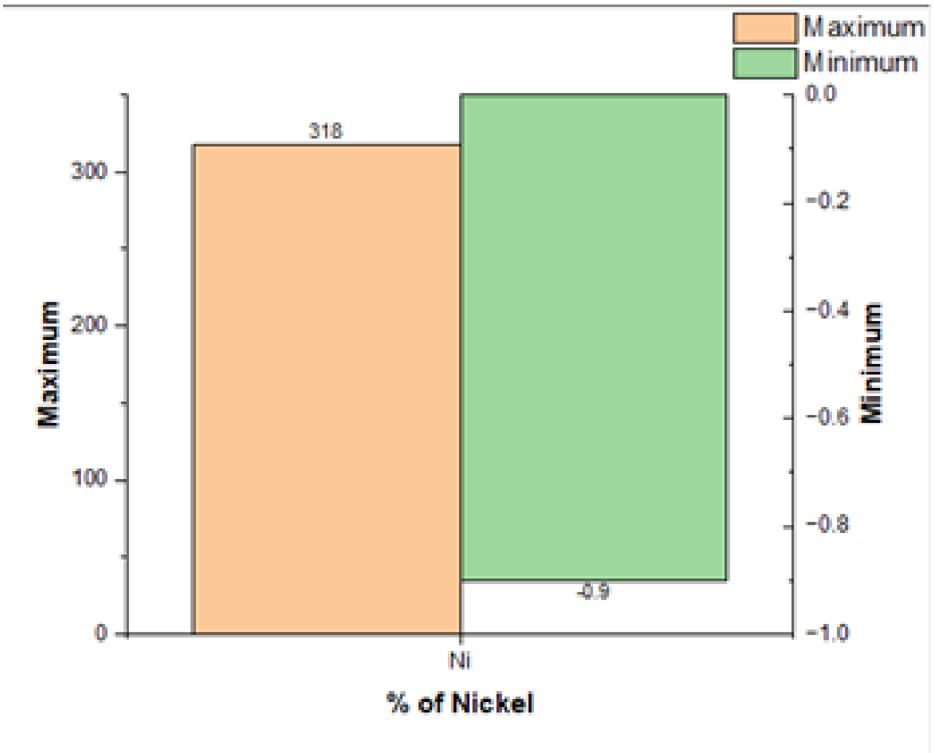


Fig 4.5. Concentration of Ni in selected children’s toys.

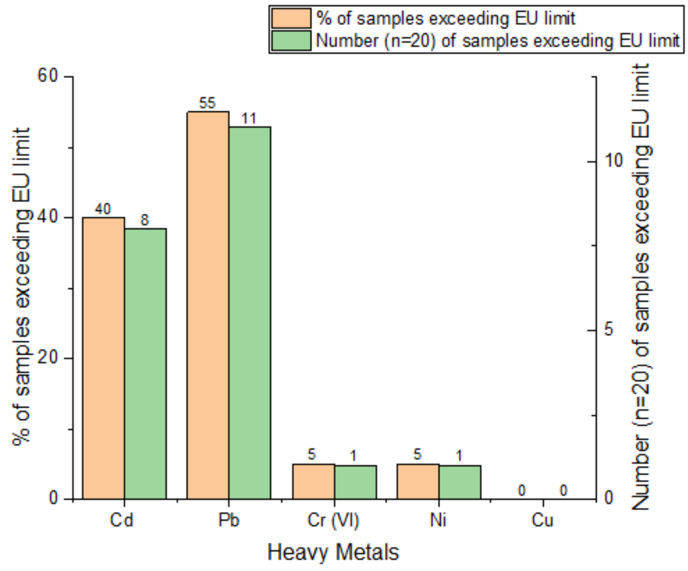
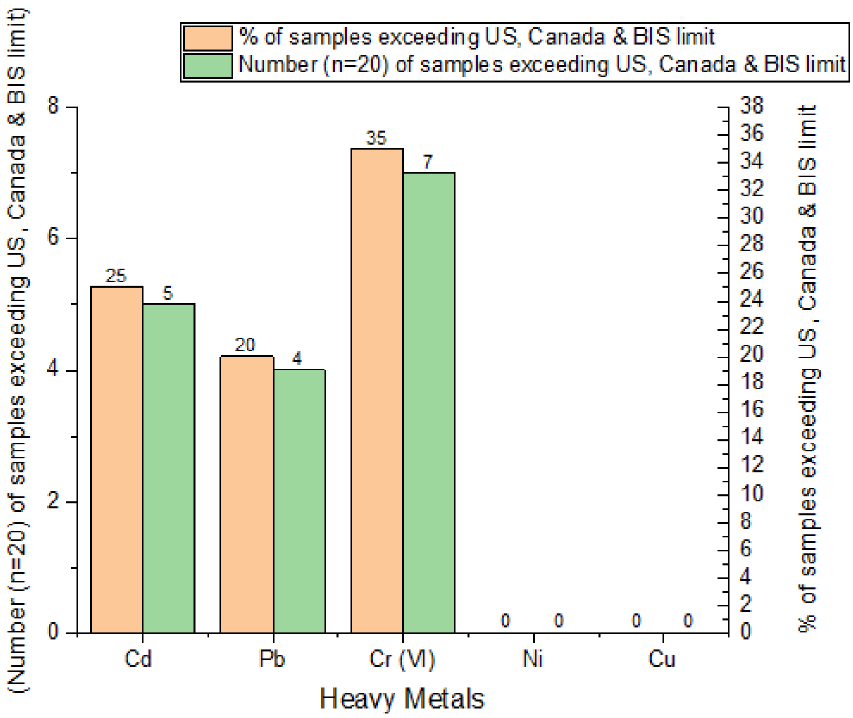


Fig 4.7. Samples (n=20) exceeding EU, US, Canadian and BIS regulation.



RESULTS

Second Part of the Study includes Questionnaire Responses

4.1.2. Exposure Evaluation by filling Questionnaire survey:

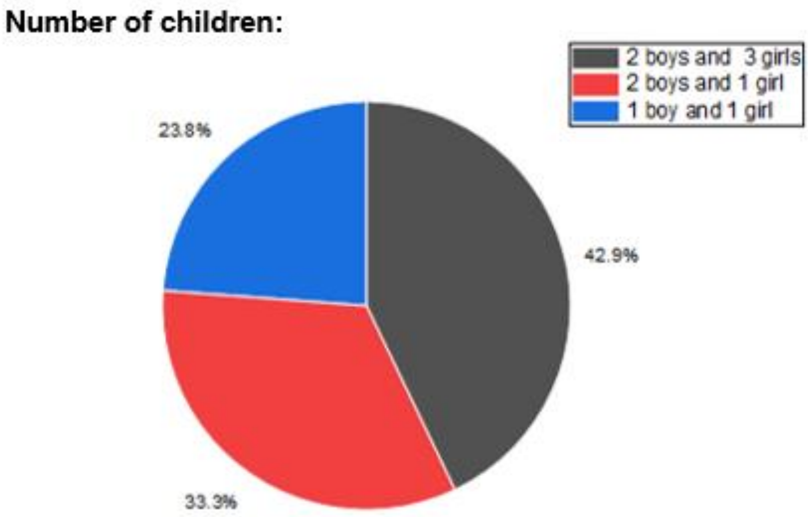
To evaluate the exposure levels of heavy metals after using toys purchased by individuals with low and average incomes pose a health risk factor or not. 50 heads of households were given a survey questionnaire, which 90% of them filled and sent back. The socioeconomic status of the family, including occupation, level of education, and money, as well as the kind and quality of the children's toys, knowledge of the health dangers connected with certain toys, and the prevalence of particular related health problems were taken into consideration while developing the questionnaire. The results are given below:

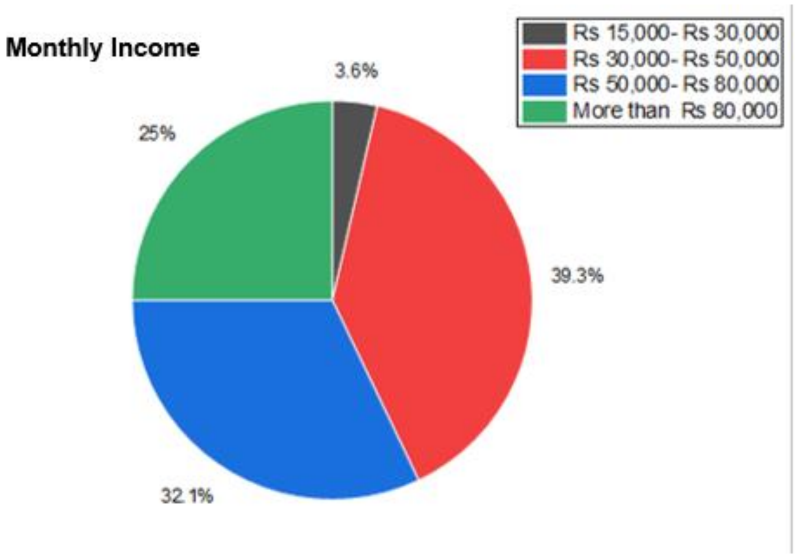
Variables	Description	percentage
Number of children	Number of toddlers.	70% parents had 1 toddler 20% had 2 toddlers 10% had 3 toddlers
	Number of girls and boys.	Around 54% parents had boys and 46% girl. 23.8% of them had 1 boy and 1 girl. 33.3% had 2 boys and 2 girls. 42.9% had 2 boys and 3 girls.
Age of youngest child	Less than 1 years	32.1%
	1-2 years	28.6%
	3-4 years	21.4%
	More than 4 years	17.8%
Range of Monthly Income	Rs 15,000-Rs 30,000	3.6%
	Rs 30,000- Rs 50,000	39.3%

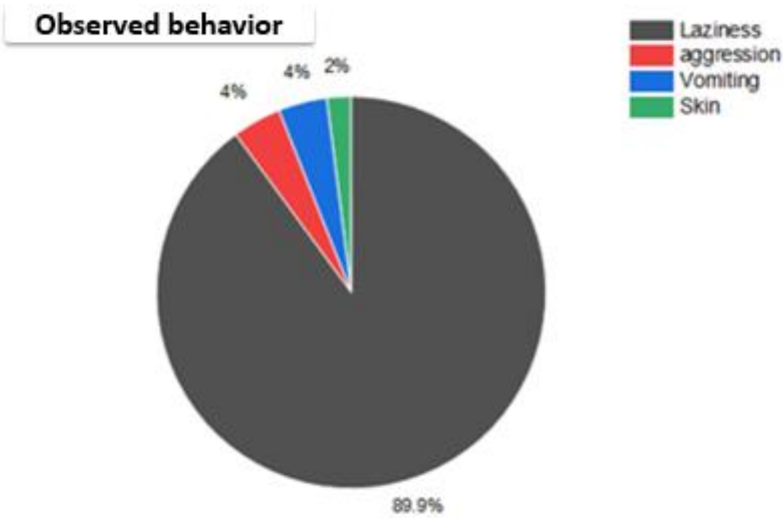
	Rs 50,000- Rs 80,000	32.1%
	More than Rs 80,000	25%
Education background	Matriculation	-
	Intermediate	14.3%
	University degree	85.7%
From where do you purchase toys?	Local toy shops	64.3%
	Labeled or branded shops	25%
	Both	10.7%
Ratio of income is spent on toys for your children?	Less than 5%	35.7%
	5-10%	32.1%
	Not estimated	32.2%
Consideration of quality of a toy while purchasing it	Price and durability	59.1%
	Educational importance	12%
	Safety	12%
	Appearance	16.9%
Your child’s most favorite toy.	Animals and character toys	37
	Transportation (cars. Jeeps, trains etc.)	23
	Blocks and puzzles	10%
	Clays and playdoughs	10.2%
	All of the above	19.8%
Awareness or consciousness of	Yes	39.3%
	No, don’t think so it’s a problem	35.7%

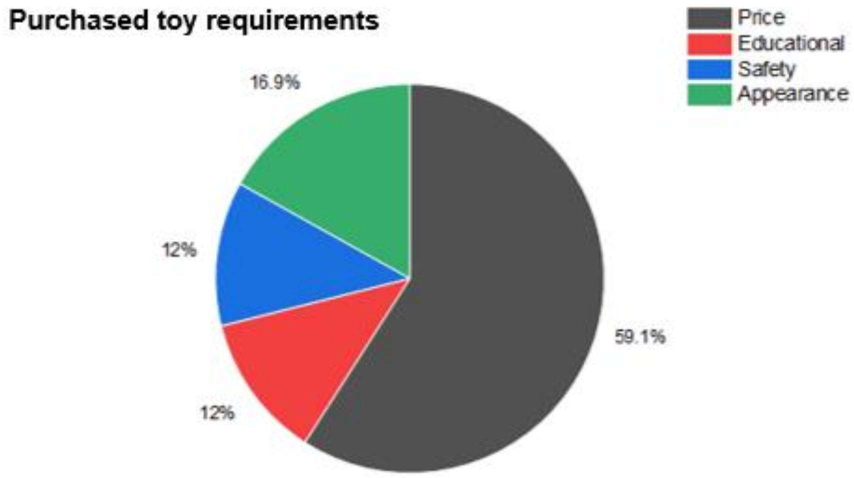
harmful impacts of chemicals used in toys? (i.e. heavy metals used to stabilize the structure of toys)	May be	25%
Observed behavior you notice in your children?	Laziness	89%
	aggression	4%
	Vomiting	4%
	Skin rash	2%
	None of the above	1%
Determining Importance of consideration of health effects of toys on children while purchasing among parents in Pakistan?	Yes	25%
	No	46.4%
	May be	28.6%
Did you ever think of the "effect of toys" on your child's health, before this survey, while purchasing toys for them?	Yes	44.4%
	No, I don’t think so it’s an issue	55.6%

Table 4.6: Exposure Evaluation by filling Questionnaire.


Number of children:
2 boys and 3 girls
2 boys and 1 girl
1 boy and 1 girl
23.8%
42.9%
33.3%


Monthly Income
Rs 15,000- Rs 30,000
Rs 30,000- Rs 50,000
Rs 50,000- Rs 80,000
More than Rs 80,000
3.6%
25%
39.3%
32.1%


Observed behavior
Laziness
aggression
Vomiting
Skin
4%
4%
2%
89.9%



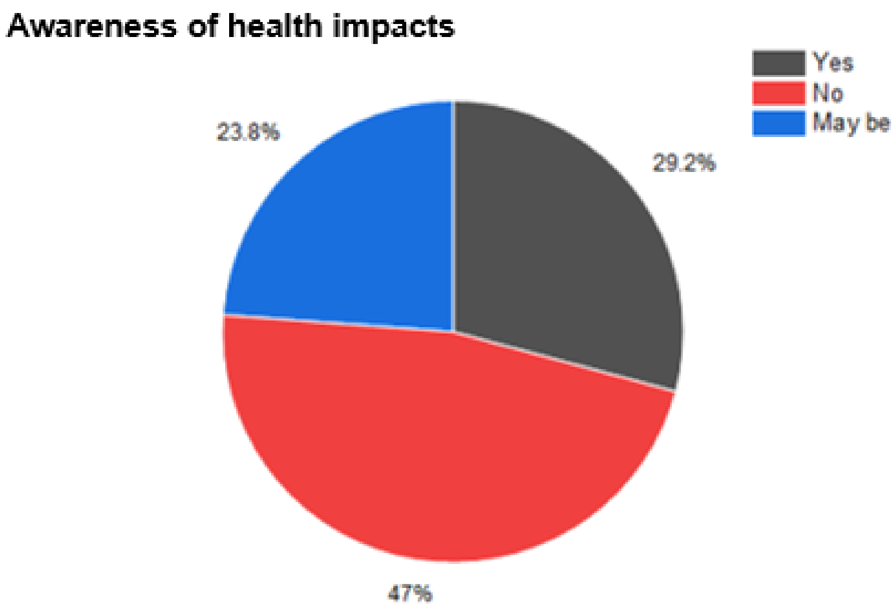


Fig 4.8. Questionnaire responses to sickness due to toys.

Results (PART 3):

Third part of the study involved dose response assessment

4.1.3. Dose-Response Assessment

Risk assessment frequently makes use of the Hazard Index (HI). To determine it, divide the average daily intake by the reference dose values from RAIS, (2013), WHO, (1993) and US EPA, (2010) as illustrated in table 3.4.

Sample labels	Samples	ADD (mg/kg/day)					HQ values				
		carcinogenic			Noncarcinogens		Carcinogenic			Non carcinogenic	
		Cd	**Pb**	**Ni**	**Cr (VI)**	**Cu**	**Cd**	**Pb**	**Ni**	**Cu**	**Cr (VI)**
Sample A	Teethers	9.35×10^-6	1.96 10^-4	-4 10^-8	6 10^-5	-1.3 10^-8	0.0094	0.056	0	0	0.002
Sample B	Rattles	-7.98×10^-8	2.4 10^-5	6.53 10^-5	9.33 10^-6	-9.3 10^-7	0	0.00685	0.00326	0	0.003
Sample C	Cars	**1.116×10^-3**	**0.0133**	5.06 10^-3	**5.64 10^-3**	2.7 10^-3	**1.116**	**3.813**	0.25	0.069	**1.88**
Sample D	Clay/ Play dough	1.86×10^-6	1.067 10^-5	3.86 10^-5	-5.33 10^-8	2.4 10^-4	0.00186	0.00304	0.0019	0.006	0.000017
Sample E	Robot characters	**9.06 10^-4**	**5.48 10^-3**	**0.04**	**0.01074**	5.8 10^-3	**0.906**	**1.56**	**2**	0.147	**3.58**
Sample F	Cartoon characters	2.146 10^-4	**2.52 10^-3**	2.133 10^-3	2 10^-5	4.12 10^-3	0.21	**0.72**	0.106	0.103	0.00667
Sample G	Animal characters	**1 10^-3**	1.045 10^-3	3 10^-3	**3.08 10^-3**	0.0109	**1.04**	0.029	0.15	0.27	**1.026**
Sample H	Plastic fruits	2.13 10^-4	5.4 10^-4	-1.33 10^-8	-6.67 10^-7	1.57 10^-3	0.21	0.15	0	0.039	0
Sample I	Dark colored Ship	**1.08 10^-3**	1.169 10^-3	5.2 10^-3	**1.36 10^-3**	6.8 10^-4	**1.08**	0.33	0.26	0.017	**0.453**
Sample J	Light colored ship	**1.006 10^-3**	6.67 10^-6	-5.3 10^-6	-1.067 10^-7	3.2 10^-4	**1.006**	0.0019	0	0.008	0
Sample K	Pacifier stars shaped (bright)	4 10^-6	6.67 10^-8	5.6 10^-5	4 10^-6	-1.06 10^-7	0.004	0.00002	0.0028	0	0.0013
Sample L	Pacifier star shaped (grey)	-1.16 10^-6	4 10^-6	11.06 10^-4	2 10^-5	2.267 10^-5	0.00116	0.0011	0.0055	0.00056	0.0067
Sample M	Green and yellow balls	-8.0 10^-8	**2.8 10^-3**	4.24 10^-3	**3.613 10^-3**	2.69 10^-3	0	**0.8**	0.212	0.067	**1.204**
Sample N	Pink and blue soccer balls	6.013 10^-4	5.2 10^-4	-1.2 10^-5	-6.67 10^-8	4.7 10^-4	0.6	0.148	0	0.01	0
Sample O	Doctor Toy Set	4.29 10^-4	3.106 10^-4	4.26 10^-5	9.33 10^-6	-6.67 10^-7	0.429	0.08	0.00213	0	0.00311
Sample P	Alphabetic toys	2.26 10^-7	3.2 10^-6	1.06 10^-5	**3.773 10^-3**	5.72 10^-3	0.000227	0.00091	0.00053	0.143	**1.257**
Sample Q	Numeric representation musical toys	4.13 10^-7	2 10^-6	1 10^-5	**1.37 10^-3**	4.35 10^-3	0.000413	0.00057	0.0005	0.108	**0.45**
Sample R	Colored blocks	2.93 10^-6	1.006 10^-3	3.86 10^-5	2.267 10^-5	1.86 10^-5	0.002933	0.28	0.0019	0.000467	0.0075
Sample S	Kitchen set	3.267 10^-4	1.11 10^-3	8.26 10^-5	2.8 10^-5	-4 10^-8	0.326	0.3	0.0041	0	0.0093
Sample T	Ringing shape toys	1.08 10^-5	-1.06 10^-7	1,89 10^-4	-2.67 10^-9	3.38 10^-3	0.0108	0	0.00946	0.0846	0

Table 4.7. Average daily doses of ingestion (ADD) in mg/kg/day and hazard quotient (HQ) in baby toys

Hazard Quotient, after calculating average daily dose was also calculated. Hazard quotient [HQ] is a ratio used to estimate the occurrence of adverse health effects that can be caused by dose. If HQ is greater than 1 then the harm is obvious and if it is lower than 1 then it is unlikely to show any harmful effects for the daily dose of the substance. Detail of which is provided in results section in tabular and graphical form.

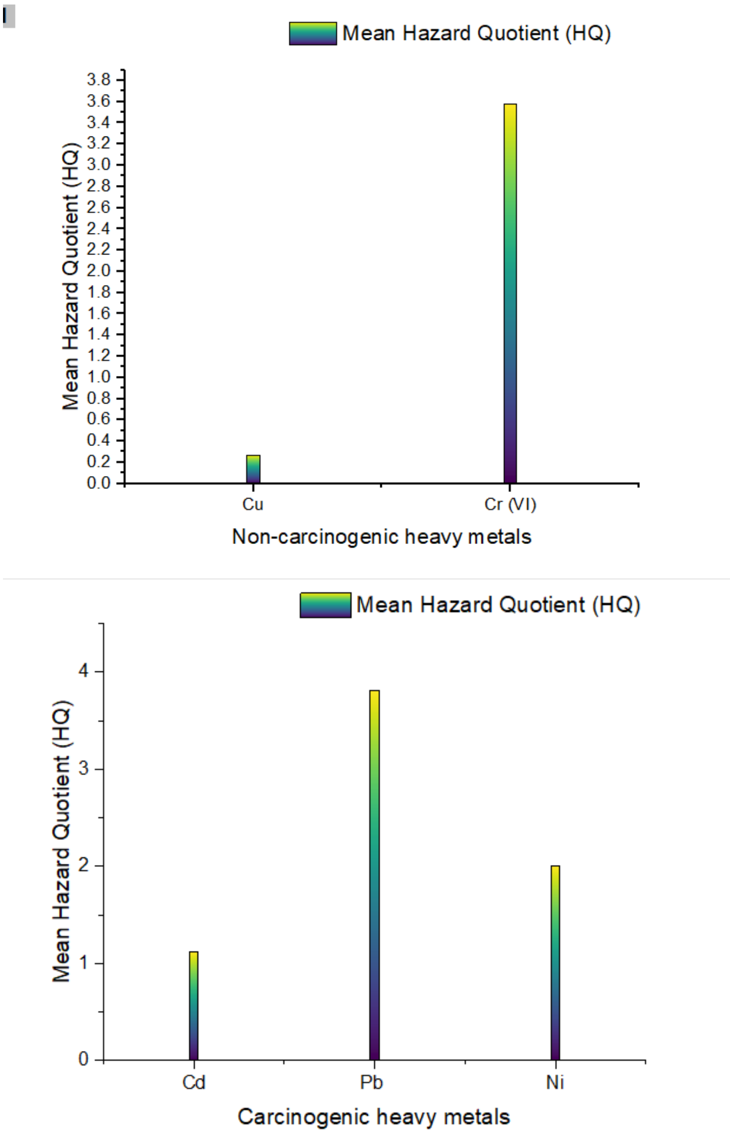


Fig 4.9. Hazard Quotient of heavy metals

The hazard quotient (HQ) values for cadmium, chromium (VI), copper, lead and nikel in baby toys range between 0-3.8. The HQ values less than 1 indicate no adverse health impact to children getting exposure till 5 years of age.

4.2. Discussion

This research focuses on the determination of metal concentration in toys by using atomic absorption spectrophotometer, comparing the results with the EU, US, Canadian and Indian regulations and the health risk assessment of metals in children toys checking whether the hazard quotient exceeds 1 or not. There is a lack of national standards for toy safety regulation in Pakistan and the absence of Pakistan standards and quality control authority regulations, specifically on toys to ensure children's safety,

All toys tested, including those shown in their respective tables in result section, contained health-hazardous elements Cd, Pb, Cu, Ni, and Cr (VI).

Cd, Pb and Ni were found in 40%, 55% and 5% samples exceeding the EU limits despite being classified as carcinogens. Cadmium toxicity in toys and baby products had also been described in other pieces of literature, including (Kumar and Pastore, 2007), (Guney and Zagury 2013). In the literature, almost similar conclusions for Pb have also been reported (Gul, et al., 2022), (M. Hillyer, 2014) and Turner, A. (2019). 35% of the samples were exceeding Cr (VI) regulatory limits of European Union. It is impossible to assess Cr (VI) oral carcinogenicity. There is no evidence in the existing literature that Cr (VI) is carcinogenic when exposed orally.

Cr (VI) and Ni were also identified at exceeded concentrations, however compared to Pb and Cd, their quantities were less. In a nutshell, there is a trend of exceeding EU regulations was Pb > Cd > Cr (VI) > Ni. Copper was not exceeding any regulation yet present in considerable amount of samples.

According to the socio-economic questionnaire responses, 54% of parents filled the survey had girls and 46% had boys. 32.1% of children were under 1 year old, 28.6% were between 1 and 2 years old, 21.4% were between 3 and 4 years old, and 17.8% were above 4 years old. The majority of the questioned homes had two boys and two girls, and about 61% of the children were under the age of four.

The health risk is deemed unacceptable when HQ > 1 and shouldn't be ignored at HQ > 1. In case of cadmium, almost all the samples of toys had high amount of cadmium and its HQ value. Cd in the Sample C, E, G, I, and J was HQ above 1 i.e. 1.16, 1.04, 1.08, and 1.006 respectively.

Sample C had the highest HQ (2.004mg/L) of cadmium and least concentration was detected in sample F. While Cr (VI), majority of samples had considerable hazard quotient of chromium (VI). Cr (VI) in the Sample C, E, G, I, M, P, and Q was HQ above 1 i.e. 1.88, 3.583, 1.026, 0.453, 1.20, 1.257, and 0.5. Lead's HQ in the Sample C, E. and M was above 1 i.e. 3.813, 1.56 and 0.8. Most of the Ni samples had negligible hazard quotient. Only sample E had high HQ value of Ni i.e. 2. Hence, a lot of samples had above 1 HQ values of cadmium, lead, nickel and chromium (VI) indicating adverse health impact on children. Copper assessment in samples had all the HQ values less than 1 indicating no adverse impact on children. Numerous researches have been looked into to demonstrate the presence of heavy metals in kid's toys (Gul, et al., 2022), (Terry Mohammed, et al., 2020), (Ismail et al., 2017) and (Korfali, S. I., Sabra, R, Jurdi, M., & Taleb, R. I. , 2013)

CONCLUSION

In short, those plastic toys were collected that were inexpensive, made for young children (infants to 5 years old), and mostly desired by low-income groups. Almost all the toys samples collected from local stores of Lahore had considerable and even high amount of Cd>Pb>Cr (VI)>Ni>Cu.

Due to the lack of regulation and controls from the regulatory system, low-cost items are readily available in local markets. However, investigations have shown that these contaminated toys are highly dangerous for children's health and may cause serious health issues and damage to their brain, kidney, bones, and nervous systems. Even a small amount in the blood may have such a negative impact on a child's health. Therefore, future research on this topic in children's toys will definitely be beneficial in creating regulations on toy samples and raise awareness among parents regarding health of their children while buying toys.

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APPENDICES

Appendix A

This form seeks feedback from (PARENTS BUYING PLASTIC TOYS FOR THEIR CHILDREN LIVING ONLY IN LAHORE) regarding the negative impact of heavy metals inside them. It focuses regarding factors like income, education level, type and quality of children's toys, and awareness of the health risks associated with particular toys. It's an interesting study that will consume 5 minutes of your valuable time. Please share your sincere, meaningful opinions.

How many toddlers/infants do you have? (Choose one option)

1-2

2-4

4-6

<6

Number of boys (choose one option)

1-2

3-4

5-6

<6

Number of girls (choose one option)

1-2

3-4

5-6

<6

Age group of your youngest kid? (choose one option)

Less than 1 year

1-2 years

3-4 years

4-5 years

What is your monthly income range? (choose one option)

Rs 1500-Rs 30,000

Rs 30,000-Rs 50,000

Rs 50,000-Rs 80,000

Rs 80,000-Rs 100,000

What percentage of your income is spent on toys for your children?

Less than 5%

5-10%

More than 10%

Not estimated (occasionally)

Your level of education?

Matriculation

Intermediate

University degree

From where do you purchase toys mostly?

Local stores

Branded stores

Both

How do you consider the quality of a toy while purchasing it? (You can select more than one option)

Your preference:

Price	Quality (Safety)	Appearance
Durability	Educational Importance	

Favorite toys of your child? (You can select more than 1 option)

Animals

Dolls/ Characters

Transportation

Blocks and puzzles

Clays and play doughs

Are you aware/conscious of harmful effects of chemicals used in toys? (i.e. heavy metals used to stabilize the structure of toys)

Yes

No

Maybe, don't think so a problem

What common behavioral changes or illness did you notice in your children, when they played with toys? (You can select more than 1 option)

Laziness

Headache

Vomiting

Skin rash

Do you think health effects of toys on children are considered important while purchasing toys among parents in Pakistan?

Yes

No

Maybe

Did you ever think of the "effect of toys" on your child's health, before this survey, while purchasing toys for them?

Yes

No