Contamination by Hazardous Elements in Low – Priced Children’s Plastic Toys Bought on the local Markets of Karachi, Pakistan

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Abstract
Children's plastics toys may contain toxic metals to which infants and young children can be orally exposed and may pose acute or chronic adverse health effects. The objectives of this research were to evaluate the total metal concentrations (TMCs) of Pb, Cd, Cr, Ni, Zn, Cu, and Mn in children's plastic toys bought in the local markets of Karachi, Pakistan, and compared TMCs to different regulatory limits. Total 44 children's plastic toys sourced in the Karachi local markets had analyzed by an atomic absorption spectrophotometer for heavy metals contaminations. These toy samples were divided into two groups; Plastic toys (DCT) and Plastic toys with paints or coatings (DPCT). For plastic toys, 83% (19) of samples had TMCs that exceeded European Union (EU) toy safety regulation limits for Pb, and 65% (15) of samples that exceeded for Cd. For plastic toys with paints or coating, 43% (9) of samples had TMCs that exceeded EU migration limits for Pb and 24% (5) for Cd. More than 20 samples exceeded the United States Consumer Product Safety Commission (U.S. CPSC), Canadian, and Bureau of Indian Standards (BIS) toy safety regulation limits. In toys samples (n = 44) very high TMCs of Pb (64%), Cd (45%), Cr (5%), and Ni (2%) were observed. Zn, Cu, and Mn TMCs were also existing but below the Regulation limits. The Contamination levels of Pb, Cd, Cr, and Ni and smaller extent of Zn, Cu, and Mn still pose health issues in children and may cause serious problems in their health.

Introduction
The research development of heavy metals is not a new area of science, having existed for more than a century. The study of heavy metals is called heavy metal science. It is a provocative field of science (Kumar Das, Singh Grewal et al. 2011). Many definitions of heavy metals have been in the literature based on atomic weight, density, physical characteristics, and chemical toxicity. Heavy metals are naturally occurring elements with a high atomic weight and five times the density of water. Heavy metals are a member of a loosely-defined subset of elements that exhibit metallic properties that includes transition metals, some metalloids, lanthanides, and actinides. It cannot be metabolized by the body, creates metal body burden, and cause metal accumulation (Yang and Massey 2019).

Human exposure to heavy metals is an important current problem. Consumer products may contain toxic chemicals which can affect consumer health and cause serious health problems, especially in young children because children are highly sensitive to exposure due to their physiological and developmental properties. Children have exposed to a certain level of metals via multiple pathways like food, air, soil, and water (Guney and Zagury 2013). Childhood exposure to environmental metals continues to be a major health concern. Hazardous elemental contamination in children's toys is a widespread problem. Children's toys may contain high levels of toxic metals. These toxic chemicals are already present in contaminated recycled material, or plastics materials which used to manufacture mostly low priced consumer goods and products, and some metals are added during the manufacturing process to provide or improve the brightness, softness, stability, and flexibility of the final product to make it more attractive for the young children (Negev, Berman et al. 2018). Use of metals as stabilizers in plastics during manufacturing, application of paint containing metal pigment in toys, and use of contaminated recycled plastic and electronic waste, or metals in toy production are the main reasons for hazardous metals contamination in children's toys (Guney and Zagury 2012). Numerous studies on toys contamination by harmful elements were report in different countries; (Greenway and Gerstenberger 2010) examined Pb in the plastic of children's toys collected from daycare centers in Las Vegas valley, Nevada. (Sindiku and Osibanjo 2011) reported the level of Pb, Cd, Cr, and Ni in the plastic components of 51 children's toys imported to Nigeria. (Ahmad, Nasibullah et al. 2012) analyzed Pb, Cd, Ni, Zn, Cr, Co, and Mn in Leachates of 26 brands of plastic toys Purchased from Different Districts of UP, India. (Guney and Zagury 2013) examined As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, and Se in 72 toys and jewelry items purchased from the North American Market. (Kang and Zhu 2014) reported Pb, Cr, As, Cu, Ni, Ba, Cd, and Sb in 35 plastic toys bought on the Beijing market. (Cui, Li et al. 2015) tested for As, Cd, Sb, Ni, and Pb in 45 children's toys and jewelry purchased from Nanjing, China. (Sobhanardakani and Babaei 2016) examined As, Pb, Cd, and Cr in 30 children's plastic toys collected from Hamadan City. (Le ha 2017) reported Zn, Cr, Cu, Ni, Mn, Pb, As, and Cd in 31 plastic toys in Hanoi, Vietnam. (Tumer 2018) analyzed As, Ba, Cd, Cr, Hg, Pb, Sb, and Se in 200 second-hand plastic toys sourced in the UK. (Issa and Alshatteri 2019) examined 14 toxic metals in 6 second-hand plastic infant items collected from markets of Kalar city, Iraq. (Mohammed, Dial et al. 2020) assessed Pb, Mn, Ni, Cr, Cd, and Cu in 11 toys and 07 baby items sold in Trinidad and Tobago.

Heavy metals are employed as additions in polymers, such as paints pigments, plasticizers, UV stabilizers, fillers, colorants, antioxidants, processing aids, and flame retardants (Godoi, Santos Jr et al. 2009, Ozbek, Ustabasi et al. 2015, Ratnakumar, De Alwis et al. 2017). Polyvinyl chloride (PVC) is the most widely used polymer; it is also used to make soft and hard toys and contains heavy metals. PVC is used in toys to stabilize polymers and prevent deterioration from sunlight, heat, and wear that causes heavy metals liberation from children's toys. Vinyl contains chlorine, which requires the inclusion of metal stabilizers. Without a stabilizer, chlorine can damage the product by producing hydrochloric acid. The Consumer Product Safety Commission (CPSC) has proven via experiments that light and heat can cause vinyl toys to degrade and produce Pb dust. However, vinyl toys discharged Pb during regular product usage (Sindiku and Osibanjo 2011). Heavy metals can be transmitted from toys when young children constantly chew, lick, and suck on their toys and consume a certain quantity of these poisonous and dangerous chemicals through their typical hand-to-mouth action. Heavy metals are weakly bonded to the surface of the painted toys, allowing them to be released and causing a hazardous impact in the long run (Guney and Zagury 2014, Cui, Li et al. 2015, Le ha 2017).
Heavy metals exposure can provide a long-term concern due to their ability to bio-accumulate. Toxic heavy metals can impair our brain functions, energy, neurological system, kidney, lungs, and other organ functioning. Pb is a neurotoxin that can cause lead poisoning, damage to the brain and nervous system, slowed growth and development, hearing and speech problems, learning disabilities, low IQ, Anemia, and kidney failure (Greenway and Gerstenberger 2010, O’Connor, Hou et al. 2018, Njati and Maguta 2019). On the other hand, cadmium (Cd) is a nephrotoxic, carcinogenic, and build of Cd in the kidney that causes kidney disease. Cd can cause a wide variety of acute and chronic effects in the neurological system and respiratory system, bone defects, kidney cancer, prostate cancer, and lung cancer (Turner 2019). Chromium (Cr) metal and Cr(III) compounds are not generally considered harmful to one's health. The most prevalent forms of chromium in the environment are Cr(III) and Cr(VI). However, hexavalent chromium is very hazardous and mutagenic when inhaled. Cr(VI) is a very active carcinogen at the cellular level. Human oral exposure to Cr(VI) causes hepatotoxicity, which may lead to primary liver cancer and increase the likelihood of cancer patients' deterioration. (Guney and Zagury 2014, Karaš and Frankowski 2018).

Zinc(Zn), Nickel(Ni), Copper(Cu), and Manganese(Mn) are essential for life and are important requirements for good health, but excess and long-term exposure can be harmful and cause health difficulties. Excessive Unnecessary Zn absorption reduces Cu and iron (Fe) absorption. The free Zn ion is a powerful Lewis acid that can be caustic. Stomach acid contains hydrochloric acid, which quickly dissolves metallic Zn to form caustic zinc chloride. Because of the high solubility of the Zn ion in the acidic stomach, this chloride can damage the stomach lining, and excessive Zn can also damage nerve receptors in the nose, causing headaches and Anosmia means partial or total loss of one's sense of smell. (Ahmad, Nasibullah et al. 2012). Long-term exposure to Ni can cause skin irritation, decreased bodyweight, heart, and liver damage (Sindiku and Osibanjo 2011, Charehsaz, GÜVEN et al. 2014). Long-term exposure to Cu can cause Wilson's disease, a rare genetic disorder that causes Cu poisoning in the body, Anemia, stomach and intestinal irritation, and liver and kidney damage (Brewer 2010). A high level of Mn causes manganism, a biphasic disorder. An inebriated individual may exhibit obsessive behaviors, sadness, psychosis, and mood swings in the early stages. Late-stage manganism, which is comparable to Parkinson's disease, develops from early neurological signs. Monotone and delayed speech, weakness, forward-leaning stride, expressionless face, inability to move backward without falling, tremor, stiffness, and general difficulties with locomotion, dexterity, and balance are all symptoms (Ahmad, Nasibullah et al. 2012).

In the past, children's exposure to hazardous elements via ingestion of many consumer products has resulted in many cases with serious acute or chronic adverse effects, including death. (Njati and Maguta 2019) reviewed some cases related to contaminated metal Pb injuries in toys from the U.S., and other countries; A girl diagnosed with seizure disorder had a toy horse which was a recall due to a high level of Pb contamination which may cause seizures. Another little girl was diagnosed to have a high Pb level in her blood, playing with toys that were recalled. Another case where a small boy's hand started itching after playing with a remote-controlled toy car that contained Pb. Another one where a little boy opened a set of toy cars after 5 minutes, developed a huge red rash over his hands, and was diagnosed with Pb poisoning. the little boy experienced breathing problems and nausea and died the following day (Njati and Maguta 2019).

Millions of toys have been recalled in recent years due to chemical safety hazards such as; In June 2007 1.5million units were recalled that violated U.S. Government standard for Pb in paints. In January 2010 CPSC recalled 55,000 units that contained high levels of Cd. In June 2010, 12million promotional drinking glasses sold at McDonald's were recalled due to painted coating contained a high level of Cd (Becker, Edwards et al. 2010). The CPSC website for recall shows that more than 18million items have been withdrawn from the market due to high Pb levels between 2007-2018 and recall data from Canada's official website included a wider list bet 2007 -2018 1.6million products have been officially recalled for Pb contamination in 138incidents (Becker, Edwards et al. 2010, Guney and Zagury 2012, Njati and Maguta 2019, Guney, Kismelyeva et al. 2020)

In Pakistan, to the author's knowledge, this is the first scientific investigation that evaluates the presence of toxic contaminations in low-priced children's plastic toys randomly collected from the local markets in Karachi. For this purpose, in the first stage, only low-priced items are selected for analysis. Present research only focuses on total metals concentration (TMCs). If TMCs will exceed high numbers, then further bioaccessibility testing is required.

Due to the absence of National based toy safety regulation limits in Pakistan, or there are no Pakistan standards and quality control authority guidelines, especially for toys to ensure children's safety. Obtained results have compared from other regulations available in different countries and regions are mentioned in Table 1. Its includes, European Union (EU) Toy Safety Directive (European Council 2009), United States Consumer Product Safety Commission (U.S.CPSC) toy safety F963-11, Canadian limits (Government of Canada,2016-2018), and Bureau of Indian Standards (BIS) IS:9873 regulation limits.

The objectives of this research are as follows:

- To evaluate the current level of contamination in low-priced children's toys (n = 44) available in Karachi local markets in terms of total metals concentrations (TMCs) (Pb, Cd, Cr, Cu, Mn, Ni, and Zn).
- To compare the TMCs results with EU, U.S., Canada, and BIS Toy safety Regulations limits.
Materials And Methods

Study Design

Forty-four samples, including twenty-three plastic toys and twenty-one plastic toys containing paint or coating samples, were selected and purchased from different local markets in Karachi, Pakistan. Samples were randomly picked from local markets, stalls, mall stores, bargain stores, roadside vendors, and retail toy shops. Selecting those plastic toys which were low priced, design for small children around 3-5 years old, and mostly demanded by low-income groups. Collected samples include; cars, soft baby toys, animals toys, balls, fruits toys, soft dolls, fishes, ships, planes type characters. All samples included in this research had grouped into two categories: children's plastic toys (DCT) and children's plastic toys with paint or coating (DPCT). All samples were coded and stored in their original packaging.

We tested for the following health-hazardous elements in terms of total metal concentration (TMCs); Lead (Pb), Cadmium (Cd), Nickel (Ni), Zinc (Zn), Chromium (Cr), Copper (Cu), and Manganese (Mn).

Sample Preparation and Analysis

Toys samples were weighted, and by using a cutter and scissors each toy body was sliced into extremely little pieces. Some samples were crushed and ground into powder. To create one composite sample for each toy, different parts of the sample were combined with different colors of the same toy and were kept in glass vials. Due to the varied sorts of toys samples, two types of sample preparation techniques were employed. Some toys were dried ash in the furnace before digestion, while others were digested straight to remove paint colors and coating. Both methods were previously reported in the literature (Hillyer, Finch et al. 2014, Mohammed, Dial et al. 2020)

Dry Ashing Method also reported (Kumar and Pastore 2007, Omolaoye, Uzairu et al. 2010, Mohammed, Dial et al. 2020) in literature was used, Toys samples were cut into small pieces and weighed into porcelain crucibles, then charred on a hot plate until fuming stopped. This was followed by 4 hours of total ashing in a muffle furnace at 350°C and then placing the crucible in a desiccator. After cooling the crucible, the sample was powdered and homogenized, and 1gm of powdered material was precisely weighted. High purity grade Nitric acid (HNO3) (65%) and hydrogen peroxide (H2O2) (30%) were added and digested. Following completion of digestion, the clear solution was cool and filtered using a Whatman 40 filter paper then made up of deionized water in a 100ml volumetric flask. All Digested Toys samples were kept at 40°C until metals analysis.

To remove the paints and coatings from the toy samples, the same techniques as described in (Hillyer, Finch et al. 2014, Finch, Hillyer et al. 2015) were used. The toy sample was placed in a beaker, HNO3 was added, and the sample was gently dipped in it. A beaker solution containing a toy sample and HNO3 was stirred with a glass rod to help this process a tiny quantity of H2O2 was also added. After removing the coating and fully digesting the sample, the toy solution was gravity filtered and the resulting mixture is diluted to the marked with deionized water into a 100ml volumetric flask and kept at 40°C until the metals analysis. To eliminate excess liquid, the remaining undissolved solid sample was rinsed and dried in a drying oven. When an undissolved solid sample was entirely dried, the difference in mass between after and before digestion was recorded, indicating the amount of toy sample effectively digested.

Standards solution, blanks, and digested samples were analyzed at Global Environmental Lab (GEL) in Karachi, Pakistan. The Atomic Absorption Spectrophotometer (AAS-Thermo Scientific Series Model iCE 3000) was used for quantitative elemental analysis.

Results And Discussion

Comparison Of Total Metal Concentrations With The EU Directive, the Canadian, the U.S., and the BIS toy safety regulation Limits

Present research only focuses on total metals concentration (TMCs). If TMCs are exceeded in high numbers, then further bioaccessibility testing is required. TMCs results are compared with the BIS, U.S., Canadian, and EU toy safety regulation limits due to the absence of national standards for toy safety regulation in Pakistan, and there are no Pakistan standards and quality control authority guidelines, especially on toys to ensure children's safety, results of the present research were compared from other regulations available in different countries and regions are mentioned in Table 1.

The results obtained from the present research are compared with European Union (EU) Toy Safety Directive (European Council 2009). In the first stage, EU limits have been used in discussion and interpretation because the EU Toy Safety Directive delivers a more comprehensive approach to the chemical safety of toys than any other regulations. After all, it differentiates the migratable limits for various types or groups of toys, namely scraped off toy material; liquid or sticky toy material; and dry, brittle, powder-like, or pliable toy material. In order to compare the TMCs, the EU limits for scraped-off toy material have been used.
Like the United States, Consumer Product Safety Commission (U.S. CPSC) adopted the American society for testing and materials (ASTM) standard for toy safety F963-11. According to ASTM F963, 100mg/kg (total) Pb limits for substrates in children's products and for surface coating its set 90mg/kg(soluble) for Pb, 75mg/kg(soluble) of surface coating and substrates other than clay for Cd and 60mg/kg(soluble) in surface coating and substrates for Cr (ASTM International 2017)

In Canada (Government of Canada 2016) sets limits for Pb in consumer products or surface coating(soluble) 90mg/kg(total) and for Cd its 1000mg/kg in surface coating (soluble) and 130mg/kg(total) (Government of Canada 2018).

In India, the Bureau of Indian Standards (BIS) is the National Standards Body of India under the Department of Consumer Affairs, Ministry of Consumer Affairs, Food & Public Distribution, Government of India. It is a statutory body established under the Bureau of Indian Standards Act, 2016. One of the main functions of BIS is to prescribe standards for covering goods and systems under the BIS regime. BIS IS:9873 regulations governing heavy metals in children's toys and set limits for Cd is 75mg/kg, Pb 90mg/kg, and Cr 60mg/kg. BIS limits are identical to U.S. limits.

In Pakistan, to the author's knowledge, this is the first scientific investigation design that evaluates the presence of toxic contaminations in low-priced children's plastic toys randomly collected from the local markets of Karachi. However, several studies have been investigated to prove heavy metals present in children's toys. Like (Kumar and Pastore 2007) found Pb and Cd in soft toys, (Godoi, Santos Jr et al. 2009) evaluated Ba, Cd, Pb, and Cr levels in the toy by using Laser-induced breakdown spectroscopy, (Greenway and Gerstenberger 2010) examined Pb level in daycare centers toys and found Pb in excess quantities, (Omolaoye, Uzairu et al. 2010) reported the levels of Pb, Cd, Ni, Cr, Cu, Zn, Co, and Mn in PVC and Non-PVC toys and high levels were obtained in PVC toys, (Sindiku and Osibanjo 2011) research indicated that Pb, Cr, Ni, and Cd found in high quantities in plastic toys, (Ahmad, Nasibullah et al. 2012) found levels of Pb, Cr, Cd, Co, Zn, Ni, and Mn in toys.(Gunev and Zagury 2013) examined different toy categories for 10 elements and reported Pb, Cu, and Cd in high Concentration along with Sb, Sc, Ba, Cr, Ni, Mn, and As were within the limits in some categories, (Hillyer, Finch et al. 2014) also reported Pb, Cd and As in toys, (Kang and Zhu 2015) Investigated Pb contained in based material of plastic toys, (Turner 2018) analyzed As, Pb, Ba, Hg, Sb, Cr and Cd in Second-hand toys and found Pb and Cd exceeded in limits, (Issa and Alshatteri 2019) also investigated second-hand children's product and high amount of Zn, Pb, Hg, and Cr detected and (Mohammed, Dial et al. 2020) also worked on children's toys to analyzed Pb, Cr, Mn, Cu, Ni, and Cd. All former literature indicated that toxic substance in children's items is in great concern and investigated time to time. Past pieces of literature also indicated that Pb and Cd are highly dangerous for children health and are neurotoxin and nephrotoxin that's why Pb and Cd are the prime focus of present research and Cr, Ni, Zn, Cu, and Mn are the secondary focus but equally important.

TMCs were detected in the present research are shown in Table 2 and 3 for DCT and DPCT groups and their minimum and maximum ranges are presented in Figure 1 and evaluated in Table 4. Health hazardous metals Pb, Cd, Ni, Cr, Zn, Cu, and Mn were found in all toys samples which are illustrated in Figure 1, it should be noted that not all elements found in this research were exceeded from regulatory limits but were present in some quantities. Seven metals were investigated however, only Pb, Cd, Ni, and Cr were exceeded from EU toy safety Regulatory limits in Table 1. Pb was detected in high quantity, In total 64% of samples exceeded from EU limits at a mean concentration of 292mg/kg are summarized in Table 4 and presented in Figure 2a. 28 out of 44 samples had levels higher than EU limits and the remaining samples were also contained Pb but their concentrations were within the permissible limits. The highest level of Pb was detected in Painted car 4 (DPCT14) 1191mg/kg, Crocodile (DCT07) 1111mg/kg, Purple car2 (DPCT01) 1011mg/kg, Elephant (DCT03) 981mg/kg, which is indicated that both groups of toys contained an extremely high level of Pb contents. Low-priced samples lead to low-quality material due to which contamination risk is also very high. For Pb, Similar results were also reported in the literature (Decharat, Maneelo et al. 2013, Hillyer, Finch et al. 2014, Kang and Zhu 2015, Turner 2018, Issa and Alshatteri 2019). Pb is used as stabilizers, coloring agents, lead(II)chromate, lead(II)carbonate, lead oxides, and lead molybdates used to produce color pigments (Isnail, Mohamad et al. 2017, O’Connor, Hou et al. 2018, Njati and Maguta 2019), basic Pb salts are commonly used as thermal stabilizers to enhance material properties and to reduced material costs like fillers in plastic manufacturing and molding process (Al-Qutob, Asafra et al. 2014, Njati and Maguta 2019). Above all, Recycle plastics are also one of the great sources of toxic contaminations, especially those obtained from electronic waste.

Cd was also detected in high quantity, In total 45% of samples exceeded from EU limits at a mean concentration of 63.24mg/kg are summarized in Table 4 and presented in Figure 2a. 20 out of 44 samples had levels higher than EU limits, and the remaining samples were also contained Cd, but their concentrations were within the permissible limits. The highest level of Cd was detected in Lion (DCT11) 459mg/kg, Blue star (DCT13) 426.1mg/kg, Horse (DCT02) 397.7mg/kg, Lion (DPCT15) 111mg/kg, which is indicated that mostly DCT samples contained more Cd than DPCT, likewise Cd based pigments are also used to color plastic material and work as a stabilizer in PVC together with the salt of Pb and Ba (Turner 2019). Many pieces of literature have also been reported for Cd Contamination in Toys and baby items included; (Kumar and Pastore 2007, Omolaoye, Uzairu et al. 2010, Gunev and Zagury 2012, Gunev and Zagury 2013, Al-Qutob, Asafra et al. 2014).

Cr and Ni were also found in exceeded levels, but as compared to Pb and Cd their quantities were less in numbers and only 5% Cr and 2% Ni exceeded from EU Limits at a mean concentration of 244mg/kg and 362mg/kg are summarized in Table 4 and presented in Figure 2a. out of
44 only 2 samples for Cr and only 1 sample for Ni exceeded from EU Limits. Cr exceeded in samples included Elephant (DCT03) 561mg/kg and Crocodile (DCT07) 479mg/kg, both of these samples were also contaminated from the high amount of Pb and Cd and also contains low levels of Zn, Ni, Cu, and Mn as Cr are also used in pigments Cr(VI) as the brightly colored yellow pigment of PbCrO4 (Tumer 2018). Ni only exceeded in 1 sample in the highest quantity that is Study boy (DCT08) 3000.1mg/kg however in that sample Pb and Cd were not detected although other elements Zn, Cr, Mn, and Cu were detected in lesser quantities. Series of experiments in past literature indicated low levels of contaminations also detected in toys that are (Leal, Catarino et al. 2016, Sobhanardakani and Babaei 2016, Karaş and Frankowski 2018, Al Kindi and Ali 2020, Mohammed, Dial et al. 2020) on the other hand in most literature levels of Zn, Cr, Ni, Cu, Mn were reported in high quantities (Al-Qutob, Asafra et al. 2014, Ismail, Mohamad et al. 2017).

TMCs results were also compared with the U.S., Canadian, and BIS Regulations are shown in Table 1. BIS and U.S. limits are identical and are shown in similar results represented in Figure 2a and combine represented in Figure 2b. In this case, Cr was higher in numbers, as in total 45% of samples were exceeded U.S. limits as well as BIS limits. 20 out of 44 samples showed a higher Cr level concerning U.S. and BIS. For Pb, 30% of samples exceeded and Cd only 16% exceeded from respected limits. 13 toys for Pb and 7 toys for Cd were exceeded out of 44 samples in total, and for Canadian limits; 30% of samples contained Pb levels were above the total or soluble limit, 13 toys samples out of 44 exceeded. For Cd soluble limits, not a single sample exceeded Canadian limits.

In Figure 2a-2b, if we compared toy safety regulations limits with TMCs, it shows that more samples contain Pb and Cd from EU Limits as compared to BIS, U.S., and Canadian limits. However, concerning BIS and U.S. limits more samples contain Cr as Cr has in higher percentage shows in Figure 2b and a lower percentage in Figure 2a. In another word, the number of toys samples comparing with EU limit Pb > Cd > Cr > Ni pattern observed Alternatively, by comparing with U.S. and BIS limits Cr > Pb > Cd pattern observed for the number of samples.

Figure 3 concludes a total number of toys samples Exceeded from toxic levels concerning EU limits of toy safety regulations which are the most comprehensive regulation in all. Total samples (n= 44) had analyzed for toxic contamination, purchased from different sites of Karachi indicated that’s 28 samples for Pb, 20 samples for Cd, 2 samples for Cr, and only 1 sample for Ni exceeded from EU limits of scraped-off toy materials, but it should be noted that all 44 samples contain some amounts of Zn, Cu, Mn, Pb, Cr, Cd, and Ni. However, their levels had not crossed the permissible limits.

**Total Metal Concentrations in low-priced plastics toys (DCT)**

DCT group contains 23 toys samples are presented in Table 2 and summarized in Table 5a. samples were coded as DCT01-DCT23, digestion was performed by using the dry ashing method as reported in (Kumar and Pastore 2007, Omoloye, Uzairu et al. 2010, Mohammed, Dial et al. 2020) and analyzed by atomic absorption spectrophotometer at Global Environmental Lab in Karachi, Pakistan.

The majority of the toys samples in the DCT group contain high levels of contamination. Overall, results were compared with different toy safety regulation limits are summarized in Table 1. 83 % of toys samples, 19 out of 23 were exceeded from EU limits of scraped-off toy material for Pb, 65% samples 15 out of 23 toys for Cd, 9% samples 2 out of 23 toys for Cr and 4% of toy 1 out of 23 toy samples for nickel were also exceeded from EU limits are summarized in Table 5a and represented in Figure 4a. The TMCs of Zn, Mn, and Cu were also detected but levels were within the EU limits. For Pb, the results of DCT03, DCT05, DCT07, and DCT18 were extremely higher in numbers. for Cd, DCT02, DCT11, and DCT13 were extremely high. For Cr, DCT03, and DCT07 and for Ni, only DCT08 was extremely higher than allowable scrap-off materials limits set by EU-Derivative. In DCT average values for Pb 205.33mg/kg, Cd 85.64mg/kg, Ni 225.92mg/kg, Cr 153.17mg/kg, Zn 220.93mg/kg, Mn 894.78mg/kg and Cu 135.66mg/kg clearly indicated metals existence in toys samples are shown in Table 5a.

On the other hand, when comparing DCT results from U.S. and BIS toy safety regulation Limits Table 1. it is notable that 26% of toys, 6 out of 23 were higher from U.S. and BIS limits for Pb, 22% of toys 3 out of 23 for Cd and 48% of toys 11 out of 23 were higher for Cr are summarized in Table 5a and represent in Figure 4b. compared to EU limits with U.S. and BIS limits results Figure 4a-4b indicates that level of Pb and Cd level was much higher in no of toys as compared to U.S. and BIS, however, Cr levels were high in no of toys with respect to U.S. and BIS and low in no of toys with respect to EU limits as shown in Figure 4a-4b. In brief, for EU limits Pb>Cd>Cr>Ni>othermetals and for U.S. and BIS Cr>Pb>Cd>othermetals patterns were observed. Meanwhile, by comparing the results from the Canadian Limits similar pattern was also observed for Pb but Cd levels were not exceeded from Canadian limits.

**Total Metal Concentrations in low-priced plastics toys with paint or coating (DPCT)**

DPCT group contains 21 toys samples are presented in Table 3 and summarized in Table 5b. samples were coded as DPCT01-DPCT21. Digestion was performed as reported in (Hillyer, Finch et al. 2014, Finch, Hillyer et al. 2015). 43% of painted toys sample 9 out of 21 for Pb and 24% samples 5 out of 21 for Cd were exceeded from EU limits for Scraped off toy materials limit are shown in Figure 5a. Ni, Cr, Zn, Cu, and Mn
were also detected but levels were within the EU limits. As compared to DCT fewer levels of contamination were observed in DPCT only Pb and Cd were exceeded in number but not a single sample was exceeded for Cr and Ni. In the same way, no Zn, Cu, and Mn were detected above the EU limits in DPCT. One of the reasons is that as Pb, Cd, Cr, Ni, and many metals are used as pigments and stabilizers in paints production (O’Connor, Hou et al. 2018, Al Kindi and Ali 2020). but toys without coatings like DCT group where more contaminations are possible due to the presence of inner matrices like filler and catalyst (Turner 2019, Al Kindi and Ali 2020, Aurisano, Huang et al. 2020) Higher results were shown for Pb in samples included DPCT01, DPCT07, DPCT11, DPCT12, DPCT14, and DPCT15, And for Cd in DPCT03, DPCT04, DPCT11, DPCT15, and DPCT16 showed the highest levels. Average values of TMCs in DPCT group for Pb 263.39mg/kg, Cd 17.86mg/kg, Ni 98.33mg/kg, Cr 65.61mg/kg, Zn 259.75mg/kg, Mn 541.90mg/kg and Cu 118.56mg/kg indicated the existence of metals in painted toys. As a pattern for toxic contamination in DPCT with respect to EU limits drawn only Pb and Cd were observed Pb>Cd>other metals.

The results compared with U.S. and BIS toy safety regulation Limits are shown in Table 1 it is indicated that 33% of paint-coated toys (7 out of 21) for Pb, 43% (9 out of 21) for Cr, and 9% (2 out of 21) painted toys samples were exceeded are represented in Figure 5b. A similar pattern of results was observed for Pb where 33% of Pb, in DPCT were exceeded Canadian limits, and 7 out of 21 toys samples exceeding from Canadian limits. By comparing no of samples from EU, BIS, U.S. and Canadian limits are shown in Figure 5a-5b summarized that with respect to EU, Pb was dominant in no of samples but with respect to U.S. and BIS limits Cr was dominant in no of samples. In brief, for EU limits Pb >Cd>othermetals whereas for U.S. and BIS limit Cr>Pb>Cd>othermetals patterns were observed.

**Conclusion**

Forty-four samples, including 23 plastic toys and 21 plastic toys containing paint or coating samples were selected and purchased from different local markets in Karachi, Pakistan. Collecting those plastic toys which were low priced, designed for small children around 3-5 years old and mostly demanded too low-income groups. All samples analyzed in the present research were grouped into two categories: children's plastic toys (DCT) and children's plastic toys with paint or coating (DPCT) and tested for Pb, Cd, Ni, Zn, Cr, Cu, and Mn contaminations in term of total metal concentration (TMCs). To the author's knowledge, this is the first scientific research design in Pakistan that assesses the presence of toxic metals contamination in children's plastic toys. However, there are no Pakistan standards and quality control authority guidelines, especially on toys to ensure children's safety in Pakistan. Therefore, Obtained results were compared from other regulations available in different countries and regions. Initially, results were compared with EU Toy Safety Regulation limits because the EU provide a more comprehensive approach and categorized toys into different groups. Pb and Cd are known as poisons, neurotoxins, and nephrotoxins that’s why both metals are the main focus of present research. Results revealed that children's toys that are present in Karachi local markets contain high levels of Pb, Cd, Ni, and Cr and minors levels of Zn, Cu, and Mn. In the DCT group, 83% Pb and 65% Cd were reported. However, In the DPCT group levels of 43% Pb and 24% Cd were detected low as compared to DCT. Overall, toys samples contain 64% Pb, 45% Cd, 5% Cr, and 2% Ni. Low priced items are easily available in local markets because of the lack of regulation and restrictions from check and balance system these contaminated toys are easily entering the markets but investigations reveal that these 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 small amount in the blood may affect child's health so badly that's why Future studies could fruitfully explore this issue further in children's toys.

**Declarations**

**Ethics approval** Not applicable.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Availability of Data and materials** All data generated or analysed during this study are included in this published article and its supplementary information files.

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**Author's Contributions**

This work was carried out in collaboration between Department of Chemistry, (University of Karachi) and Globel Environmental Lab (pvt) Limited. Authors DSG and AKT managed the literature searches. Sampling strategy, collection, sorting, investigation and samples preparation were performed by DSG and AG. Elemental analysis was performed by MAM. Statistical analysis, interpretation, calculations and editing were
performend by AG and DSG under the assistance of TA. The first draft of the manuscript were written by DSG and AG, later on revised by AKT and TA. DSG completed his M.Phil. degree from UOK under the supervision of AKT. All authors read and approved the final manuscript.

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### Tables

**Table 1. Toy safety regulations limits according to EU (Europen Council 2009), USA (U.S.CPSC) (ASTM International 2017), Canada (Government of Canada 2011,2018), and BIS (Bureau of Indian Standard 1999).**

| Heavy Metals | EU migratable limits (mg/kg) | USA (U.S.CPSC) (mg/kg) | Canada (mg/kg) | BIS (1999) (mg/kg) |
|--------------|------------------------------|------------------------|----------------|-------------------|
|               | Liquid or sticky toy material | Scraped-off toy material | Dry, brittle, powder-like or pliable material | Children's products | Surface coatings and substrates other than modeling clay included as a part of a toy (soluble) | Modeling calys included as a part of a toy (soluble) | Jewelry (total) | Surface coating material in toys (soluble) | Consumer products |
| Pb           | 0.5                          | 23                     | 2              | 100 (total)     | 90                    | 90                      | 90                   | 90 (total) | 90 |
| Cd           | 0.3                          | 17                     | 1.3            | 200 ug          | 75                    | 50                      | -                    | 1000 | 130 | 75 |
| Cr           | 9.4                          | 460                    | 37.5           | -               | 60                    | 25                      | -                    | -    | -   | 60 |
| Ni           | 18.8                         | 930                    | 75             | -               | -                     | -                       | -                    | -    | -   | - |
| Cu           | 156                          | 7700                   | 622.5          | -               | -                     | -                       | -                    | -    | -   | - |
| Zn           | 938                          | 46000                  | 3750           | -               | -                     | -                       | -                    | -    | -   | - |
| Mn           | 300                          | 15000                  | 1200           | -               | -                     | -                       | -                    | -    | -   | - |

**Table 2. Concentrations (mg/kg) of heavy metals in low-priced children’s plastics toys (DCT).**
| No. | Sample Code | Description     | Pb  | Cd  | Ni  | Cr  | Zn  | Mn  | Cu  |
|-----|-------------|-----------------|-----|-----|-----|-----|-----|-----|-----|
|     |             | EU - Limit (Scraped-off toy material) mg/kg | 23  | 17  | 930 | 460 | 46,000 | 15,000 | 7700 |
| 1   | DCT01       | Small baby boy  | 191 | 69  | 161 | 321 | 50.1 | 1871 | 311 |
| 2   | DCT02       | Horse           | 117.9 | 397.7 | ND  | ND  | 210.1 | 27.2 | 821.3 |
| 3   | DCT03       | Elephant        | 981 | 42  | 211 | 561 | 91  | 1111 | 109 |
| 4   | DCT04       | Banana          | ND  | 21  | 229 | 431 | 100.5 | 972 | 121 |
| 5   | DCT05       | Duck            | 791 | 9.6 | 122 | 339 | 81  | 1211 | 91  |
| 6   | DCT06       | Rabbit 1        | 39.6 | 7.4 | ND  | ND  | 677 | 17.4 | 39.8 |
| 7   | DCT07       | Crocodile       | 1111 | 50.1 | 412 | 479 | 111 | 3209 | 99  |
| 8   | DCT08       | Study boy       | ND  | ND  | 3000.1 | 291 | 122 | 1811 | 451 |
| 9   | DCT09       | Study girl      | 28.1 | 4.2 | ND  | ND  | 874.2 | 17.2 | 55.5 |
| 10  | DCT10       | Apple           | 29.3 | 59.7 | ND  | ND  | 74.2 | 18.2 | 59  |
| 11  | DCT11       | Lion            | 32.0 | 459 | ND  | ND  | 110.6 | 19  | 80  |
| 12  | DCT12       | Pineapple       | 41.5 | 36.9 | ND  | ND  | 82.6 | 17.6 | 42.3 |
| 13  | DCT13       | Blue star       | 38.1 | 426.1 | ND  | ND  | 98.0 | 18.2 | 43.9 |
| 14  | DCT14       | Big deer        | 36.1 | 10.7 | ND  | ND  | 1036.4 | 24.7 | 29.9 |
| 15  | DCT15       | Octopus         | 38.7 | 5.1 | ND  | ND  | 806.7 | 27.4 | 50.5 |
| 16  | DCT16       | Rabbit 2        | 36.1 | 92.5 | ND  | ND  | 155.5 | 15.9 | 53.7 |
| 17  | DCT17       | Blue ball       | 39.1 | 93.4 | ND  | ND  | 63.9 | 24.2 | 34.8 |
| 18  | DCT18       | Yellow ball     | 971 | ND  | 310.2 | 333 | 91  | 1921 | ND  |
| 19  | DCT19       | Kitty           | 41  | 31  | 110.4 | 219 | 51  | 1091 | 91  |
| 20  | DCT20       | Pink ball       | 18.3 | 43.1 | ND  | ND  | 100.6 | 14  | 36.6 |
| 21  | DCT21       | Green ball      | 61  | ND  | 320.5 | 209 | 41  | 2342 | 209 |
| 22  | DCT22       | Leach fish      | 81  | 61  | 129 | 111 | 21  | 3241 | 291 |
| 23  | DCT23       | Camel           | ND  | 50.4 | 191 | 229 | 32  | 1559 | ND  |

Table 4. Descriptive statistics representation (mg/kg) in low-priced children's toys (DCT + DPCT n = 44) with percentages of total toy samples exceed from different regulations limits.

Table 5. Comparison of total metal concentrations results from different toy safety regulations limits.
| No. | Sample Code | Description                | Pb  | Cd   | Ni  | Cr   | Zn   | Mn   | Cu   |
|-----|-------------|----------------------------|-----|------|-----|------|------|------|------|
| 1   | DPCT01      | Purple car                 | 1011| ND   | 322 | 92   | 60.1 | 891  | 109  |
| 2   | DPCT02      | White train                | 0.6 | 0.6  | ND  | ND   | 57.5 | 3.3  | 25   |
| 3   | DPCT03      | Painted car 1              | 101 | 29   | 344 | 119  | 121  | 781  | 61   |
| 4   | DPCT04      | Blue ship                  | ND  | 81   | 392 | 101  | 231  | 689  | 52   |
| 5   | DPCT05      | Yellow orange hen          | ND  | 0.5  | ND  | ND   | 22.8 | 0.9  | 23   |
| 6   | DPCT06      | Yellow airplane            | 2.1 | 1.4  | ND  | ND   | 44.1 | 2.1  | 5.5  |
| 7   | DPCT07      | Painted car 2              | 761 | ND   | 191 | 91   | 421  | 992  | 209  |
| 8   | DPCT08      | Orange duck                | 1.3 | 0.4  | ND  | ND   | 28.9 | 2.3  | 3.0  |
| 9   | DPCT09      | Pink buffalo               | 3.1 | 0.3  | ND  | ND   | 37.9 | ND   | 13.1 |
| 10  | DPCT10      | Green car                  | 0.6 | 0.6  | ND  | ND   | 41.5 | 3.6  | 11.2 |
| 11  | DPCT11      | White zebra                | 911 | 71   | 113 | 161  | 72   | 489  | 412  |
| 12  | DPCT12      | Painted car 3              | 868 | ND   | 211 | 141  | 91   | 121  | ND   |
| 13  | DPCT13      | Eye spotted wolf           | 26  | 2.5  | ND  | ND   | 498  | ND   | 26.7 |
| 14  | DPCT14      | Painted car 4              | 1191| 09   | 122 | 251  | 109  | 981  | 81   |
| 15  | DPCT15      | Lion                       | 611 | 111  | 219 | 211  | 111  | 99   | 89   |
| 16  | DPCT16      | Silver car                 | 20.1| 51   | 151 | 211  | 161  | 1161 | 61   |
| 17  | DPCT17      | Painted car 5              | 23.5| 15.1 | ND  | ND   | 679  | 1021 | 215.2|
| 18  | DPCT18      | Red fish                   | ND  | ND   | ND  | ND   | 723.4| ND   | 313.5|
| 19  | DPCT19      | Green frog                 | ND  | 0.7  | ND  | ND   | 606.4| 1390.1| 322.4|
| 20  | DPCT20      | Orange green Turtle        | ND  | 0.5  | ND  | ND   | 673.2| 1365.3| 203.0|
| 21  | DPCT21      | Yellow star                | ND  | 0.6  | ND  | ND   | 665.0| 1387.4| 254.2|
### Heavy Metals

|                | Pb   | Cd   | Cr   | Zn   | Cu   | Ni   | Mn   |
|----------------|------|------|------|------|------|------|------|
| Minimum        | 0.62 | 0.34 | 90   | 20   | 3.07 | 110  | 0.96 |
| Maximum        | 1190 | 459.01 | 560 | 1036.48 | 821.35 | 3000 | 3240 |
| Average        | 292.68 | 63.24 | 244 | 239.06 | 136.67 | 110  | 3779.25 |
| Sd             | 413.62 | 114.31 | 133.94 | 282.54 | 159.73 | 628.09 | 884.54 |
| %RSD           | 141.31 | 180.74 | 54.89 | 118.18 | 116.87 | 173.5 | 113.51 |

### Total Toy (n=44) Sample Exceed From EU Limits

| Detection          | 64% (28) | 45% (20) | 5% (2) | -   | -   | 2% (1) | -   |

### Total Toys (n=44) Sample Exceed From BIS

| Detection          | 30% (13) | 16% (7) | 45% (20) | -   | -   | -   | -   |

### Total Toys (n=44) Sample Exceed From U.S. CPSC limits

| Detection          | 30% (13) | 16% (7) | 45% (20) | -   | -   | -   | -   |

### Total Toys (n=44) Sample Exceed From Canadian Limits

| Detection          | 30% (13) | -   | -   | -   | -   | -   | -   |

#### a) Comparison of total metal concentrations of detected metals in low-priced children's plastics toys DCT group (n=23):

| Detected Metals   | Pb        | Cd        | Ni       | Cr       | Zn        | Mn        | Cu       |
|-------------------|-----------|-----------|----------|----------|-----------|-----------|----------|
| Average           | 205.3391  | 85.64783  | 225.9217 | 153.1739 | 220.9304  | 894.7826  | 135.6652 |
| SD                | 361.2576  | 138.6225  | 617.8567 | 185.8919 | 302.278   | 1079.018  | 185.8307 |
| %RSD              | 175.9322  | 161.8517  | 273.4826 | 121.36   | 136.8205  | 120.59    | 136.9774 |
| %Samples Exceed from EU-Limit | 83% (19) | 65% (15) | 4% (1)   | 9% (2)   | -         | -         | -        |
| %Samples Exceed from U.S. Limit | 26% (6)  | 13% (3)   | -        | 48% (11) | -         | -         | -        |
| %Samples Exceed from Canadian Limit | 26% (6)  | -         | -        | -        | -         | -         | -        |
| %Samples Exceed from BIS Limit   | 26% (6)  | 13% (3)   | -        | 48% (11) | -         | -         | -        |

#### b) Comparison of total metal concentrations of detected metals in low-priced children's plastics toys DPCT group (n=21):

| Detected Metals   | Pb        | Cd        | Ni       | Cr       | Zn        | Mn        | Cu       |
|-------------------|-----------|-----------|----------|----------|-----------|-----------|----------|
| Average           | 263.3952  | 17.86676  | 98.33333 | 65.61905 | 259.7524  | 541.9048  | 118.5619 |
| SD                | 420.1976  | 32.38902  | 132.673  | 86.17684 | 264.6514  | 549.2437  | 124.7605 |
| %RSD              | 159.5312  | 181.2818  | 134.9217 | 131.329  | 101.886   | 101.3543  | 105.2281 |
| %Samples Exceed from EU-Limit | 43% (9)   | 24% (5)   | -        | -        | -         | -         | -        |
| %Samples Exceed from U.S. Limit | 33% (7)  | 9% (2)    | -        | 43% (9)  | -         | -         | -        |
| %Samples Exceed from Canadian Limit | 33% (7)  | -         | -        | -        | -         | -         | -        |
| %Sample Exceed from BIS Limit   | 33% (7)  | 9% (2)    | -        | 43% (9)  | -         | -         | -        |

### Figures
Figure 1

Minimum to maximum range of elements detected in toys samples.

Figure 2

Comparison of total metal concentrations of detected metals in low-priced children's toys (n=44) 2a) no of toys samples percentages exceed from EU regulation limits in total samples. 2b) no of samples percentages exceed from U.S. and BIS regulations limits in total samples.
Figure 3

Representation of no of samples exceeds from toxic levels with respect to EU limits.

Figure 4a

Comparison of total metal concentrations of detected metals in low-priced children's toys (n=44) 2a) no of toys samples percentages exceed from EU regulation limits in total samples.

Figure 4b

Comparison of total metal concentrations of detected metals in low-priced children's toys (n=44) 2b) no of samples percentages exceed from U.S. and BIS regulations limits in total samples.
Figure 5

Comparison of total metal concentrations of detected metals in low-priced children's plastics toys DPCT group (n= 21) 5a) no of toy samples percentages exceed from EU- Toy safety regulations limits in DPCT group. 5b) no of toy samples percentages exceed from U.S. and BIS toy safety regulations limits in DPCT group.