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Study on Heavy Metal Speciation and Health Implication from Plastic Toys in Hanoi, Vietnam

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Abstract: *Children exposure to heavy metals continues to be the major health concern. This study examines the total concentration and speciation of heavy metals of 31 plastic toy samples purchased in Hanoi, which were analyzed by ICP-MS. The results showed that all plastic toy samples revealed Zn (742.48 mg/kg), Cr (99.21 mg/kg), Ni (54.12 mg/kg), Mn (46.69 mg/kg), Cu (98.5 mg/kg), As (9.58 mg/kg), Pb (28.99 mg/kg) and Cd (6.16 mg/kg), respectively. The total concentrations of heavy metal were decreased in the order Zn> Cr>Cu>Ni> Mn>Pb>As>Cd. Sequential extraction was used for finding the fraction of heavy metals in all toy samples found that major proportion of heavy metals were associated with the residual fraction. Therefore, the dominant existence of heavy metals was in the immobile phase in all toy samples. The immobile phase of heavy metals was not readily bioavailable. However, Cd was found in the most exchangeable fraction. Thus, cancer risks were up 1.76×10^{-6} and 2.29×10^{-6}, whereas non-cancer risks were 1.63×10^{-2} and 2.25×10^{-2} via digestion and dermal pathway for both targeted children (1- 3 years) and (3–5 years), respectively. All exposures posed low to moderate risk on health and ingestion was main exposure route.*

Keywords: *Cancer risk, Children toys, Hanoi metropolis, Heath risk, Speciation.*

1. INTRODUCTION

Children were particularly sensitive to toxic contaminant exposure during playing with toys were already exposed to certain levels of heavy metal via digestion, dermal contact [1]. The presence of heavy metal in children's plastic toys represented severe risks to the children due to long-term toxicological effects. Highly toxic lead (Pb), Cadmium (Cd), as well as Copper (Cu), Nickel (Ni), Arsenic (As), Chromium (Cr) can pose the hazard to children due to their presence in children's toys [1, 2]. Exposure to Pb causes impairment of cognitive development in children [2, 3]. Exposure to As and Cd may cause neural development problems and behavioral disorbents in children [3]. Chronic ingestion exposure to Cr may induce tumor in small intestine and is considered as carcinogenic substance [4].

Metals can be released from children's toys to gastric and intestinal fluids following ingestion. Routes of ingestion can be direct and also licking, sucking, mouthing and hand to mouth behavior. These activities could result in the migration of the metals from the toy material matrix through saliva. Children's exposure to toys via saliva may cause unacceptable hazard risk. Cr and Pb levels found in plastic which can come from lead chromate and chromic chloride used as pigments to make yellow and green color can be mobilized through saliva and pose a threat to children's health during mouth contact [2, 8].

The mobility and bioavailability of metals in toys depend mostly on the chemical forms in which the metal exits, rather than on the total concentration. Sequential extraction methods can define readily mobile, less mobile and immobile fractions. The three step procedure was developed by the Standards, and measurements and testing programme of European Union [5]. This method extracts water soluble and exchangeable, reducible (Fe/Mn oxide-bound) and oxidisable (organic and sulphide bound) fractions. In these methods, the water soluble + exchangeable fraction is considered readily mobile and used as an estimation of bioavailability under carcinogenic and non-carcinogenic risk.

In Hanoi, the demand of children toys has been increased for the recent years. Besides, toy goods with cheap price often enter Vietnamese markets without restriction, control and standard, especially plastic toys, has becoming popular. It is impossible to control and guarantee toy's quality that can threaten the children's health. However, heavy metal contaminants in plastic toys and health risk assessment have not been investigated comprehensively in Hanoi.

The main objective of this study is to: (1) identify the heavy metal concentration in plastic toys in Hanoi, (2) define the chemical form of heavy metal and (3) evaluate human hazard to carcinogenic and non-carcinogenic exposure through multiply pathway. These results will provide an important insight to heavy metal contamination and are conductive to the scientific society, the local enterprises and policy makers of the municipality for toy management.

2. CHEMICALS AND METHODS

2.1 Sample/Questionnaire collection

Thirty one plastic toys labelled "Made in China" were purchased in some markets in Hanoi. There were randomly selected from shops selling toys wholesale, retail and stalls considering accessibility from low to middle income. Some were soft and easily squeezable while others were not flexible enough. The inclusion criteria for the many of the items were designed for children (1-5 years), colorful and inexpensive children's plastic toys. All toys were washed, dried in room and further ground, crushed and sieved through under 2 mm nylon sieve to ensure efficient extraction. 300 questionnaires was obtained from some kindergartens and householders to get comprehensive information such as children's behavior, weight, habits and exposure time as well as toy's style that used for health risk assessment in this study.

2.2 Preparation and analysis

All chemical agents are high purity grade. The sample treatment and analysis method used for children's plastic toys in accordance with Vietnamese standard TCVN 6238-3:2011 and US.EPA 200.8. The appropriate amount of milled samples was digested by a mixture of 3ml sulfuric acid (H_2SO_4 96%) and 4ml nitric acid (HNO_3 65%) and 1ml hydrogen fluoride (HF), sequentially in the microwave Ethos 900. After completing digestion, the samples were analyzed by ICP-MS, Elan DRCe, Perkin Elmer.

2.3 Sequential extraction method

Sequential extraction of heavy metal was conducted according to the Standards, Measurements and Testing program of the European Union [5, 13]. In this procedure, exchangeable and water and weak-acid soluble metals were extracted first by acetic acid (0.1M, pH 2.85), followed by extraction of reducible metal fraction by hydroxylamine hydrochloride (0.1M, pH 2) and finally, extraction of oxidisable metal fraction by hydrogen peroxide (8.8M)/ammonium acetate (1M, pH 2). The metal concentrations of the extracts were similarly determined by ICP-MS, Elan DRCe, Perkin Elmer.

2.4 Quality control

Accepted recoveries for eight heavy metals ranged between 91.9% and 109.2%. To verify the accuracy of sequential extraction procedure, the samples were also used as certified reference material. The recovery ranges of Cd, As, Pb, Cr, Zn, Mn, Ni and Zn in the exchange fractions (F1), reducial fraction (F2), oxidisable fraction (F3) were 98.58-102.13%; 96.12-102.55%; 99.7-102.45%; 99.6-102.45%; 89.65-99.12%; 98.3-110.02%, 89.12-98.45%; 97.8-100.7%, respectively. Calibration curves for all metals are linear with correlation coefficient (R^2 > 0.999). Three replicates were performed for each sample. Sample blanks were also analyzed and subtracted every tenth sample.

2.5 Health risk assessment

The health risk assessment of each potential toxic metal is usually based on the quantification of the risk level and is expressed on carcinogenic or a non-carcinogenic health risk. The two principal toxicity risk factors evaluated are the slop factor (SF) for carcinogenic risk characterization and the reference dose (RfD) for non-carcinogenic characterization [6]. The estimation of the magnitude, frequency an duration of human exposure to each potentially toxic metal is typically reported as average daily dose. The children are exposed to plastic toy through two main pathways: ingestion and dermal contact with heavy metal in plastic toys. The average daily dose (ADD) through ingestion and dermal contact intake with heavy metal in plastic toys is calculated in equation 1 and 2. For carcinogenic and non-carcinogenic risk assessment, Incremental Lifetime Cancer Risk (ILCR) and Hazard Index (HI) are calculated according to equation 3 and 4.

$$D_{dermal} = \frac{(C_s \times CF \times AF_{skin} \times ABS_{dermal} \times SA \times EV \times EF \times ED)}{BW \times AT} \quad [1]$$

$$D_{ingestion} = \frac{(C_s \times IR_s \times EF \times ED)}{BW \times AT} \quad [2]$$

$$ILCR = \sum_{i=1}^{n} D_i \times CSF_i \quad [3]$$

$$HI = \sum HQ = \frac{D_{Dermal} + D_{Ingestion}}{RfD} \quad [4]$$

Where, D_{dermal}, $D_{ingestion}$: Daily dose in dermal, ingestion route (mg/kg.day). CSF: carcinogenic slope factors (1.5-As, $8.5.10^{-3}$-Pb, 2.10^{-2}-Ni) mg/kg.day, respectively[6]. Cs: Concentration heavy meal in mobility form (mg/kg)[this study]. SA: dermal surface exposure (6030 and 7310 cm^2 for child (1-3 years) and (3-5 years), respectively)[6,7]. EV: event frequency (1 event/day)[6]. AF_{skin}: the dermal adherence factor (0.2 mg/cm^2 for children)[6,7]. CF: conversion factor (10^{-6} kg/mg)[6]. ABSd: dermal adsorption fraction (0.03-As) and (0.001-Pb,Ni)[7]. EF: exposure frequency (365 day/year)[6,7]. ED: exposure duration (3-5) years (this study). AT: averaging time (Non-carcinogenic effects AT= ED×365 days/year. Carcinogenic effects AT = 70 years×365 days/year)[6, 7]. BW: body weight ((13.5 kg (1-3 years) and 18.55 kg (3-5 years)) [this study]. IR: intake rate (200 mg/day for children) [6,7]. RfD: chronic reference dose (1.0×10^{-3}-Cd; 4.0×10^{-2}-Cu; 3.0×10^{-1}-Zn and 3.0×10^{-3}-Cr mg/kg.day), respectively [7]. HI: Chronic hazard index (HI > 1 shows that there is a chance that non-carcinogenic risk may occur, and when HI < 1 the reverse applies). Cancer risk between 10^{-6} and 10^{-4} indicates moderate health risk, while greater than 10^{-4} suggests high potential health risk [11, 7].

2.6 Statistical analysis

Statistical analyses were performed using IBM SPSS software version 20. A probability level of $P < 0.05$ was considered statically significant.

3. RESULTS AND DISCUSIONS

3.1 Total heavy metals concentrations

The different levels of heavy metal were detected in all plastic toys purchased in Hanoi and presented in Table 1. The total heavy metals (As, Cd, Pb, Cu, Zn, Mn, Ni and Cr) in all plastic toy samples displayed in wide range from 1.84–30; 0.27–86.48, 0.86–440.45; 2.35–642.69; 22.71–7752.69; 9.68–188.33; 9.11–210.09 and 17.45–303.04 mg/kg, respectively. The mean levels of each heavy metal revealed in different samples with increased order as follows: Cd (6.16 mg/kg) < As (9.58 mg/kg) < Pb (28.99 mg/kg) < Mn (46.69 mg/kg) < Ni (54.12 mg/kg) < Cu (98.5 mg/kg) < Cr (99.21 mg/kg) < Zn (742.48 mg/kg). Such heavy metals found in all samples referred that Pb, Ni and Cd formally used as thermal stabilizers to enhance material properties, produce pigments and reduce material costs in plastic [2, 8, 10]. Furthermore, As, Cr were also used as the pigment [2,8]. In 31 analyzed plastic toys, the levels of Cd, Pb and As were slightly higher than the allowable Vietnamese standard of safety of toy (TCVN 6238) in three samples and those of Cr exceeded with allowable TCVN 6238 in twenty samples. It is likely, As was known Paris Green (copper aceto-arsenite) as pigment, whereas, Cr was valuable dye as a coloring for PVC materials as well heat stabilizer. Some colorants from Cr were $Pb(Cr,S)O_4$ and $Pb(Cr,S,Mo)O_4$ leading to yellow and red colors and Zn has recently been commonly used to enhance plastic structure and anticorrosive pigment in coating to replace Pb and Cd due to their toxicity [8,16]. Zn could be in plastic toys in the form of zinc borate or zinc omadine and was much elevated in this study. Among observed toy samples, two luminescent toys were significantly distinguished due to the highest value of Zn and Cu. This may be due to using Zn as stabilizers, colorants (yellow and light green), Moreover, ZnS also can use as a substrate and copper used for luminous intensity enhancement [16]. The levels of Pb in plastic toys in this study were much lower than those in Nigeria and Thailand, whereas, those of Ni, Cr, and Zn were higher [8, 12].

Table 1: *Concentration of eight heavy metals (mg/kg) of plastic toys from Hanoi markets (n=31)*

Heavy metals	Minimum (mg/kg)	Maximum (mg/kg)	Average (mg/kg)	TCVN 6238
As	1.84	30.00	9.58	25
Cd	0.27	86.48	6.16	75
Pb	0.86	440.45	28.99	90
Cu	2.35	642.69	98.50	-
Zn	22.71	7752.69	742.48	-
Mn	9.68	188.33	46.69	-
Ni	9.11	210.09	54.12	-
Cr	17.45	303.04	99.21	60

(-: not indicated)

3.2 Heavy metal speciation

Following the sequential extraction procedure described in Section 2.3, the percentages of heavy metal associated with each fraction were performed in Figure 1. The results revealed that eight heavy metals occurred in all samples existed in exchangeable (F1), reducible (F2), oxidisable (F3) and residual (F4), in which residual form (F4) accounted up the majority.

For first step of sequential extraction procedures, the acid soluble fraction (F1) of metals are weakly associated with carbonates that is subject to ion exchange. This form is easy to migrate and transform under acidic conditions that is very sensitive for children though saliva when children take mouth behavior [6]. Children's exposure to toys via saliva may cause unacceptable hazard risk. This form is readily mobile that is used as an estimation of bioavailability and risk calculation [12, 13]. The results presented that the order of association with F1 was observed for each heavy metals: Cd > Mn = Cu > Ni > Zn > Pb > Cr > As. Mobile fraction as a percentage was lowest for As (1.9%) and highest for Cd (11.93%) that agreed with other studies [13, 14]. Cadmium was highest mobility and well known due to highly toxic effects on health that raise concerns.

The second fraction of reducible metals (F2) indicated the metals usually associated with Fe and Mn oxy/hydroxides that was difficult to release due to strong ionic wrapping. This fraction were observed in order as Cd > As > Mn > Cu > Ni > Pb = Zn > Cr. Cadmium and Arsenic were mainly associated with the reducible fraction accounted up 16.83% and 17.77% of their total concentration, respectively. Despite their low percentage associated in F2, the health risk of human damage from heavy metals cannot ruled out.

The sequential fraction is an oxidisable fraction (F3) that bound to organic matter and sulphide. Under oxidizing condition, organic matter degradation can lead to the release of the metals bounds to this fraction. The organic fraction released during the extraction process is not bioavailable since it existed in stable humic substances that releases small amounts of metals slowly [13, 14]. The results have shown a low percentage of F3 of all heavy metal, except for Cd and Cr. The low content of metals associated with F3 might be due to the small amount of organic matter [14].

The fourth step showed a fraction of metals associated with residuals. This fraction is most stable and has no bioavailability. All heavy metals existed in this fraction, in which Pb and Zn were dominated. The percentage residual fractions decrease in order: Pb > Zn > Ni > As = Cu > Cr > Mn > Cd.

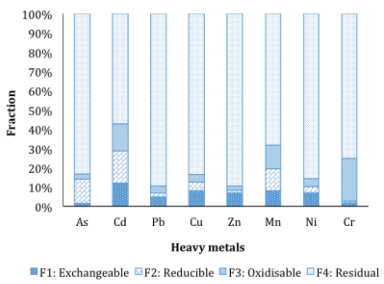


Fig 1: *The distribution of different geochemical fractions of heavy metals in toys in Hanoi*

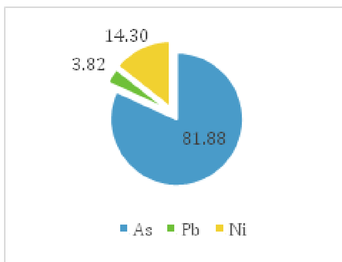
3.3 Health risk assessment

Exposure was assessed by oral and dermal pathway during children's playing activities with plastic toys at home and school. The study identified the potential risk (carcinogenic and non-carcinogenic risk) due to the exposure of children to heavy metals. The cancer risk is formulated for As, Pb and Ni, whereas the non-cancer riskI) is calculated for Cu, Cr, Ni and Cd. The quantitative carcinogenic (ILCR) and non-carcinogenic risk was the summation of individual risks of each heavy metal through each route, presented in Table 2.

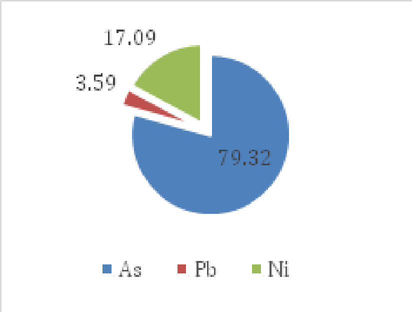
Table 2: *Calculations of Hazard Index (HI) and life time cancer (ILCR) of chemical Toys from Hanoi markets*

Routes	ILCR		HI	
	1-3 years	3-5 years	1-3 years	3-5 years
Dermal	1.93×10^{-7}	3.91×10^{-7}	3.44×10^{-3}	6.95×10^{-3}
Ingestion	1.57×10^{-6}	1.90×10^{-6}	1.28×10^{-2}	1.56×10^{-2}
Sum	1.76×10^{-6}	2.29×10^{-6}	1.63×10^{-2}	2.25×10^{-2}

The cancer risk levels for children (1-3 years) via ingestion and dermal contacts were 1.57×10^{-6} and 1.93×10^{-7}, respectively, while those for children (3-5 years) were 1.9×10^{-6}, 3.91×10^{-7}. Cancer risk of dermal route of children was lower than ingestion route and ingestion appeared to be predominant exposure route for both children (1-3 and 3-5 years). These findings were consistent with previous studies in Canada and India [1, 15]. Cancer risk between 10^{-6} and 10^{-4} indicate moderate health risk, while lower than 10^{-6} suggests low potential health risk [7]. The total cancer risk is the sum of risk occurred from ingestion and dermal exposure route. In this study, the total cancer risk for children (1-3 years) and (3-5 years) were up 1.76×10^{-6} and 2.29×10^{-6}, respectively, which indicates a moderate potential cancer risk. The cancer risks of children at two age range were insignificantly distinguished. However, the children were very vulnerable due to high physical contacts (hand and mouth) with the toys that raised concern. Otherwise, the total non-cancer risk for children via both ingestion and dermal pathway were approximately similar, in which, ingestion route was also dominated. The HI values for children (1-3 years) and (3-5 years) were up 1.63×10^{-2} and 2.25×10^{-2}, respectively, posing low risk.



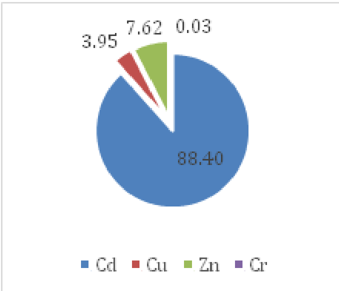
(a)



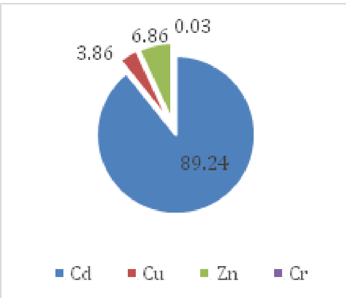
(b)

Fig 2: *Contribution of heavy metal on cancer risk for groups (1-3 years) and (3-5 years) (a,b)*

The contributions of individual heavy metal on risk assessment were also observed in all samples. The contributors on both cancer and non-cancer risks were different and showed in Fig.2 & 3. The contribution percentage of individual heavy on risk cancer risk were followed in the same trend in both targeted children (1-3 years) and (3-5 years) as in order: As > Ni > Pb (Fig. -2 a,b). For non-cancer risk, the contributions were followed in order: Cd > Cu> Zn > Cr for both targeted children (Fig. -3 a,b).



(a)



(b)

Fig 3: *Contribution of heavy metal on non-cancer risk for group (1-3 years) and (3-5 years) (a,b)*

The findings revealed that the main contributors on cancer and non-cancer risk were As and Cd, respectively, for both children group. While Cd was a major contributor on non-cancer risk for plastic toys in Vietnam and Canada [1], Pb and Ni were predominant in Thailand and India [12, 15]. There are also some uncertainty in this calculation since the RfD values for some metals are based on the total amount of intake, including uptake from toys and other sources. However, the RfD values from other sources usually cannot be accurately estimated. Therefore, calculation of HI using RfD may underestimate the risk. Furthermore, a more detailed risk assessment for exposure is also recommended.

4. CONCLUSION

The plastic toys purchased from various markets in Hanoi contained toxic heavy metals (As, Pb, Zn, Ni, Cd, Cu, Cr and Mn) with wide concentration ranges. The levels of Cr were higher than TCVN 6238 in twenty toys. Especially, two luminescent toys were distinguished due to the highest value of Zn and Cu. All toy samples remained majority in residual fraction (F4). Cd was most mobility (F1) and As was inverse. Cd and As were mainly associated with the reducible fraction (F2). Minor percentage of heavy metal existed in oxidizable fraction (F3) except Cr and . The total cancer risk and non-cancer risk for children (1 - 3 years, 3 - 5 years) posed low to moderate risk, and the ingestion was main exposure route for these children. As is a predominant contributor on cancer risk, whereas, Cd is dominant on non-cancer risk. The children (1-3 years, 3-5 years) was very sensitive due to high physical contacts (hand and mouth) with toys who need to be concerned in the society. The adopted approach in this study is very useful in determining overall toxicity of heavy metal in children's toy.

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