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Full Length Research Paper

Heavy metal assessment of some soft plastic toys imported into Nigeria from China

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Chinese made toys were analyzed to determine the levels of heavy metals (Pb, Cd, Ni, Cu, Zn, Cr, Co and Mn) in the products. Toy samples were randomly selected from products available in the shops at Zaria, Kano and Kaduna markets in Nigeria. The toy samples were tested for PVC before analysis. After digestion with concentrated acids (HNO_3 and H_2O_2), concentrations of the selected heavy metals were determined in triplicate using a flame atomic absorption spectrophotometer. 75% of the toys samples tested positive for PVC. Concentrations of heavy metals in the toys ranged from 2.50 - 1445.00, 0.50 - 373.33, 31.17 - 119.67, 12.00 - 93.67, 266.67 - 2043.33, 5.00 - 191.67, 1.00 - 73.33 and 6.17 - 36.67 μgg^{-1}, for Pb, Cd, Ni, Cu, Zn, Cr, Co and Mn respectively. Both PVC and non-PVC toys contain heavy metals but the concentration of these metals in non-PVC toys are generally less than that of PVC toys. The present study reveals that 17% of the toy samples show high concentration (above USFDA limit) of Lead, Cadmium, Chromium and other metals determined; this poses a threat to children exposed to such toys.

Key words: Heavy metal, toys, polyvinyl chloride.

INTRODUCTION

It is well known that metals such as Lead and Cadmium are toxic, especially to young children; however, toys as well as other consumer products still contain these metals. Toys are integral part of children developmental processes. Besides providing entertainment to children, toys also serve as educational materials for them. A toy may mean different things to children of different age groups and hence exposure pathways also differ accordingly. A child below 3 years of age may handle a toy in a completely different manner from a child 3 - 6 years of age. Toys can broadly be categorized as mechanical, electrical and soft toys (Abhay and Prashant, 2007). Toys may also inflict accidental injuries to children. Sharp edges of toys or other electrical, mechanical or flammable characteristics may cause accidents. Chemical exposure to children, especially from toys, is an emerging concern. Metals in materials and paints are loosely bound to the surface and can leach easily. Lead poisoning from toys causes learning disabilities, kidney failure, anemia and irreversible brain damage in children (WorldNet Daily, 2009). The chewing, licking and swallowing behavior of children is a common source of lead and cadmium exposure (Kelly et al., 1993). Children and pregnant women are particularly susceptible to lead poisoning. The digestive system of children absorbs up to 50% of the lead they ingest (National Referral Centre, 2009). In fact, physicians and scientists agree that no level of lead in blood is safe or normal (National Referral centre, 2009). Toys that are made of Polyvinyl Chloride (PVC) are potential source of risks to children. Polyvinyl Chloride, a leading chlorine containing plastic, is a polymer or a large chain-like molecule, made up of repeating units of Vinyl Chloride (a monomer), and commonly referred to as Vinyl or PVC. It is one of the most commonly used materials in the consumer marketplace. It is used in packaging, construction and automotive material, all categories of products, including toys, and medical equipment (Figure 1).

PVC has a special problem of auto- digestion since free chlorine radicals in the structure reacts with free hydrogen radicals forming HCl (hydrochloric acid) leading to the digestion of PVC, which causes a chain

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Figure 1. A picture showing how the hand-to-mouth behavior of a child can expose him to heavy metals in toys.

reaction and proceeds rapidly to completely loose strength (causing damage to manufacturing equipment as well). Lead or Cadmium is hence added to PVC as stabilizers, to prevent the free chlorine radicals from reacting with hydrogen radicals to form HCl (Tuczai and Cortolano, 1992). Lead compounds are the most common stabilizers in PVC. Some of them are: Basic lead carbonate, lead stearate, basic lead stearate, tribasic lead stearate, basic (dibasic) lead stearate, and basic lead phthalate. Other metals have also been used when lead came under regulatory scrutiny, which include Cd, Zn, organotins etc. Lead and Cadmium are also added into PVC or other plastic products as colouring agents in form of organo-metallic compounds. What is noteworthy here is that, unlike popular perceptions, metal stabilizers are not bound to the polymer, but freely available to leach out over time or in response to light, chewing etc. So toys made up of PVC when chewed or sucked by children put them at a risk of severe exposure to lead and cadmium.

Although, numerous investigations have been carried out on health impacts of lead and other heavy metals on humans, little has been done to ascertain their source in children environment in Nigeria (Needleman, 2007). Heavy metals have mostly been studied in soil, water, paints, and food (Sharma et al., 2005; Tripathi et al., 1997; Malviya et al., 2001). Toys which are intimately linked to children's environment have not really been investigated as one of the sources of Lead, Cadmium and other heavy metals. The absence of any known study on heavy metals in toys coupled with the fact that these materials dominate the children environment propels the need for this study. This study was designed to ascertain the levels of lead, cadmium, chromium, nickel, zinc, copper, cobalt and manganese in soft plastic toys. The toy samples were collected from Zaria, Kano, and Kaduna markets in Nigeria. These toys were not manufactured in Nigeria but imported from China. A total of 12 toy samples were purchased.

MATERIALS AND METHODS

The toy samples were first subjected to an indicative test for Polyvinylchloride (PVC) using the Beilstein test. This is a preliminary test for PVC. The Beilstein test is based on the principle that copper halides vapourize readily giving off a blue-green coloured flame owing to the presence of copper (Mohrig et al., 1998). All toy samples which tested positive for Beilstein test were further tested for total content of heavy metals. A few toy samples which gave negative test for Beilstein test were also tested for the total content of heavy metals. A total of 12 samples (9 tested positive for Beilstein test and 3 tested negative for the test) were analyzed for lead, cadmium, chromium, nickel, zinc, copper, cobalt and manganese.

The methodology involves subjecting samples first to ashing to breakdown the PVC and then digesting in accordance with EPA SW-846 3050 as reported by Abhay and Prashant, 2007. Individual samples broken down into pieces in a large silica crucible were charred on a hot plate till the fume ceased to exist, followed by complete ashing in murfle furnace. The crucible was then taken out

Table 1. Mean (±SD) heavy metal concentration (ugg^{-1}) in toy samples.

Toy samples	Metals							
	Pb	Cd	Ni	Cu	Zn	Cr	Co	Mn
Feeding bottle	6.50 ± 1.33	0.5 ± 0.00	36.17 ± 0.29	14.83 ± 1.55	370.00 ± 10.00	8.33 ± 2.89	1.00 ± 0.00	6.50 ± 1.32
Bird	19.33 ± 1.61	1.50 ± 0.00	37.00 ± 1.73	43.00 ± 2.29	425 ± 18.03	8.23 ± 2.89	0.00 ± 0.00	17.83 ± 1.32
Baby 1	22.50 ± 1.50	7.67 ± 0.58	80.50 ± 2.78	32.67 ± 1.25	741.67 ± 2.89	5.00 ± 0.00	6.17 ± 0.29	7.17 ± 1.04
Ring a bell	376.67 ± 20.82	40.82 ± 0.76	119.67 ± 1.76	74.33 ± 1.26	1083.33 ± 41.63	191.67 ± 14.43	43.33 ± 2.89	36.67 ±2.89
Building block	2.83 ± 0.58	2.33 ± 0.58	15.33 ± 1.15	12.00 ± 0.87	266.67 ± 12.58	ND	ND	6.17 ± 0.29
Dice	2.50 ± 0.50	ND	38.00 ± 6.08	18.17 ± 1.26	325.83 ± 13.77	ND	2.17 ± 0.58	8.17 ± 1.26
Toad	39.83 ± 2.26	5.83 ± 0.29	95.17 ± 0.76	67.67 ± 5.29	928.33 ± 5.77	5.00 ± 0.00	9.33 ± 0.29	16.67 ± 0.29
Horse	28.33 ± 2.36	16.83 ± 0.76	36.83 ± 0.58	93.67 ± 1.76	820.17 ± 6.53	ND	6.17 ± 0.29	7.83 ± 0.29
Butterfly	22.00 ± 1.00	34.50 ± 3.77	45.50 ± 3.78	31.33 ± 0.58	663.50 ± 5.67	13.32 ± 2.89	11.67 ± 5.77	14.17 ± 0.76
Squeaky baby	1445.00 ± 60.83	373.33 ± 2.89	35.50 ± 2.29	29.33 ± 2.47	2043.33 ± 16.07	130.00 ± 26.46	73.33 ± 2.58	13.00 ± 1.26
Basket ball	6.33 ± 0.29	1.50 ± 0.00	31.17 ± 1.26	33.17 ± 1.44	360.00 ± 15.00	15.00 ± 0.00	9.50 ± 0.50	14.38 ± 0.76
Baby 2	25.33 ± 1.04	63.17 ± 0.58	76.50 ± 3.97	36.17 ± 1.26	1176.33 ± 25.23	15.00 ± 0.00	ND	18.67 ± 0.76

ND-Not detected.

of the furnace and kept in desiccators for cooling. After cooling, the samples were powdered and homogenized in the silica crucible. Then 1 g of the sample was taken in separate silica crucible for acid digestion. Analar grade Nitric acid (65%) and Hydrogen peroxide (30%) were used for digestion in an open vessel. The digest was filtered through a Whatman 41 filter paper to remove the insoluble particles and brought to a final volume of 50 ml with distilled deionized water. Blank sample was also prepared similarly. Glass wares, crucibles and plastic containers were washed with liquid soaps, rinsed with distilled water and soaked in 10% HNO_3 for 24 h; cleaned with distilled-deionized water and in such a manner that no contamination occurred (Adnan, 2003).

Standards were prepared with serial dilution technique within the range of 0.5 - 2.5 ppm for lead, cadmium, nickel and manganese, 1 – 5 ppm for copper and cobalt, 0.5 – 2 ppm for zinc and 2 – 10 ppm for chromium. The standards used were analar grade, BDH. The instrument was first calibrated with stock solutions of the prepared standards before analysis. The final processed samples were quantitatively analyzed using Buck Scientific VGP 210 Flame Atomic Absorption Spectrophotometer. After every five samples analyzed using AAS, the first sample was repeated for quality check. Only when the results were within 10% of earlier readings did the analysis proceed further. The data obtained in this study were analyzed using Pearson correlation analysis and Duncan's one way analysis of variance.

RESULTS AND DISCUSSION

The results of heavy metal concentration in the toy samples are presented in Table 1. All the toy samples analyzed were found to contain lead, nickel, copper, zinc and manganese in varying concentrations. Cadmium was detected in all the toy samples except in dice. Chromium was detected in three out of the twelve toy samples. Cobalt was not detected in three samples. The results ranged from 2.50 - 1445.00, 0.50 - 373.33, 31.17 - 119.67, 12.00 - 93.67, 266.67 - 2043.33, 5.00 - 191.67, 1.00 -73.33 and 6.17 - 36.67 µgg^{-1}, for Pb, Cd, Ni, Cu, Zn, Cr, Co and Mn respectively. Both PVC and non-PVC toys contain heavy metals but the concentration of these metals in non-PVC toys are generally lower than that of PVC toys. This may be due to absence of salts of these metals in the polymer material as stabilizer but they are present as impurities. Lead and Cadmium are generally of higher concentration in "Squeaky baby" and "Ring a bell" than other samples. These toy samples ("Squeaky baby" and "Ring a bell") have outer coating paint which might have led to increase in the concentration levels of these metals in them.

A correlation matrix for heavy metals in the toy samples was calculated to see if some metals were interrelated with each other and the results are presented in Table 2.

A strong positive correlation at $P < 0.1$ between Pb and Cd, Zn, Cr, and Co; Cd and Zn, Cr and Co was obtained. This indicates a significant influence of one metal on another. It also suggests the possibility of the metals coming from the same source. Because the correlation coefficient between Pb and Cd in the toy samples was statistically significant (0.971), it can then be argued that Pb and Cd were used as stabilizers in toys. A weak negative correlation was observed

Table 2. Correlation among heavy metals in toys.

	Pb	Cd	Ni	Cu	Zn	Cr	Co	Mn
Pb	1							
Cd	0.971	1						
Ni	-0.003	-0.085	1					
Cu	-0.014	-0.085	0.511	1				
Zn	0.848	0.872	0.349	0.280	1			
Cr	0.697	0.562	0.478	0.270	0.641	1		
Co	0.946	0.868	0.205	0.149	0.827	0.857	1	
Mn	0.183	0.074	0.717	0.468	0.339	0.741	0.408	1

between Pb and Ni (-0.003), Pb and Cu (-0.014), Cd and Ni (-0.085) and Cd and Cu (-0.085). This suggests that changes in the level of one of these metals would not affect the concentration of the other in toy.

Analysis of variance (ANOVA) showed significant variation ($P < 0.05$) between toy samples for some of the heavy metals determined (Table 3). For instance, concentration of lead in Squeaky baby (1445.00 μgg^{-1}) is significantly different from that of the other samples. Also, concentration of chromium in "Ring a bell" (191.67 μgg^{-1}) is significantly different from that of other samples. There is no significant difference between levels of lead and cadmium in feeding bottle, bird, building blocks, dice and basket ball.

Abhay and Prashant (2007) determined the concentration of lead and cadmium in samples collected from three cities in India. The average results obtained are 27.8, 20.67 and 278.73 μgg^{-1} for lead and 26.53, 3.10 and 2.61 μgg^{-1} for cadmium in Delhi, Chennai and Mumbai respectively. The results are comparable to that obtained in this study but the maximum concentration of lead (2104 μgg^{-1}) is higher than (1445.00 μgg^{-1}) of this study. Joseph (1996) reported a Greenpeace study on Lead and Cadmium in children's vinyl products. The study expanded to include 10 major U.S. cities and all the vinyl products tested were found to have lead and cadmium in varying concentrations.

Regulations exist which provides limits in materials for which surface contact with children can result in possible ingestion. Analysis of toys and other items of interest for heavy metal content is necessary to validate their manufacture, distribution and sale. The European standard for safety of toys, EN 71, part 3, which is adopted into ISO 8124-3, contains one section entitled "Migration of certain elements". In this section, it defines the limits of elements migration from toy materials. Only 2 (Ring a bell and Squeaky baby) out of 12 (17%) samples analyzed in this study exceeded the limit set for Lead (90 μgg^{-1}) and Chromium (60 μgg^{-1}). Only one sample (Squeaky baby) exceeded the limit for Cadmium (75 μgg^{-1}). It was observed that 2 samples (Ring a bell and Squeaky baby) are very toxic and this indicates that it is possible that other similar products are still in the toy market. Such high quantities of heavy metals in toys pose a threat to children's health. It must be noted that exposure from lead is in addition to that of other toxic metals. Hence, children playing with toys having these metals are exposed to health risk.

Concentration of lead in toys and other products marketed to children under the age of 12 was limited to 300 μgg^{-1} (CPSC, 2009). The maximum limit for Lead in Vinyl formally recommended by the Consumer Product Safety Commision for Vinyl miniblinds is (200 ppm) (CPSC, 1996).

Conclusion

The present study reveals that both PVC and non-PVC Chinese made toys contain heavy metals in varying concentration. However, the levels of these metals in PVC toys are generally higher that non-PVC toys. This confirms that the use of PVC plastic in making toys contributes toxic metals to the toys. 17% of the toy samples show high concentration of lead, cadmium, chromium and other metals determined; this poses a threat to children exposed to such toys. Therefore, with all toys samples containing these heavy metals in varying concentration and some even showing high concentration, our results show that Chinese toys are potential source risk to children's health.

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Table 3. Duncan's one way analysis of variance (ANOVA) of means for heavy metal concentration (ugg^{-1}) in toy samples ($P < 0.05$).

Metals	Samples											
	Feeding bottle	Bird	Baby 1	Ring a bell	Building blocks	Dice	Toad	Horse	Butterfly	Squeaky baby	Basket ball	Baby 2
Pb	6.50^{ac}	19.33^{ac}	22.50^{ac}	376.67^{b}	2.83^{a}	2.50^{a}	39.83^{c}	28.33^{ac}	22.00^{ac}	1445.00^{d}	6.33^{ac}	25.33^{ac}
Cd	0.50^{a}	1.50^{a}	7.67^{b}	40.82^{c}	2.33^{a}	ND^{a}	5.83^{b}	16.83^{d}	34.50^{e}	373.33^{f}	1.50^{a}	63.17^{g}
Ni	36.17^{ag}	37.00^{ag}	80.50^{b}	119.67^{c}	15.33^{d}	38.00^{ag}	95.17^{e}	36.83^{ag}	45.50^{f}	35.50^{g}	31.17^{g}	76.50^{b}
Cu	14.83^{ae}	43.00^{b}	32.67^{chi}	74.33^{d}	12.00^{a}	18.17^{ae}	67.67^{f}	93.67^{g}	31.33^{ch}	29.33^{c}	33.17^{hi}	36.17^{i}
Zn	370.00^{a}	425.00^{b}	741.67^{c}	1083.33^{d}	266.67^{e}	325.83^{f}	928.33^{g}	820.17^{h}	663.50^{i}	2043.3^{j}	360.00^{a}	1176.33^{k}
Cr	8.33^{a}	8.33^{a}	5.00^{a}	191.67^{b}	ND^{a}	ND^{a}	5.00^{a}	ND^{a}	13.32^{a}	130.00^{c}	15.00^{a}	15.00^{a}
Co	1.00^{a}	ND^{a}	6.17^{acd}	43.33^{b}	ND^{a}	2.17^{a}	9.33^{cd}	6.17^{acd}	11.67^{d}	73.33^{e}	9.5^{cd}	ND^{a}
Mn	6.50^{a}	17.83^{b}	7.17^{a}	36.67^{c}	6.17^{a}	8.17^{a}	16.67^{b}	7.83^{a}	14.17^{d}	13.00^{d}	14.38^{d}	18.67^{b}

Means with the same superscript in the same row are not significantly different. ND-Not detected.

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