Metal Leaching: Release from Kindergarten Books in Simulated Saliva Conditions

S. C. Onuchukwu[1*], J. I. Ogubuike[2], P. I. Eche[3] and P. P. Idiong[4]

[1.] Department of Chemistry, University of Uyo, Uyo, Akwa Ibom State, and Faculty of Science and Computing, Amadeus University Amizi, Ikwuano, Abia state. onuchukwuchiemela@gmail.com
[2.] Department of Chemical Sciences, University of Hundderfield, Queensgate, United Kingdom. ogubuikegoodyear@gmail.com
[3.] Department of Chemistry, University of Uyo, Uyo, Akwa Ibom State, Nigeria
[4.] Department of Biochemistry, Faculty of Science, University of Port Harcourt, Nigeria.

ABSTRACT

The leaching of metals from consumer products, especially those intended for children, poses significant health risks, particularly during prolonged exposure. This study investigates the release of metals from kindergarten books under conditions mimicking saliva, simulating real-world interactions where children may explore books orally. The experiment, conducted in a controlled lab, exposed books to a saliva-like solution for various time periods. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to quantify toxic metal concentrations (As, Cd, Cu, Ni, Pb). Results showed concentrations of toxic metals (mg/kg) ranging from 2.85 to 40.7 for As, 1.83 to 38.9 for Cd, 9.78 to 159 for Cu, 2.85 to 11.2 for Ni, and 36.1 to 111 for Pb. Correlation analysis revealed a significant positive correlation between As and Ni. Saline extraction produced no detectable As in some samples, while Cu was found in all. Stomach acid extraction showed varying levels of Pb, As, and Cu, indicating potential health risks. The health index (HI) for most samples exceeded 0.1 for As, Cu, and Pb, with As having the highest HI values. These findings highlight the risks of metal migration from printed materials and the need for safer alternatives in children's educational resources.

Key words: Leaching, Toxic metals, Kindergarten books, Saliva simulation, Health risks

INTRODUCTION

Children possess distinct physiological and developmental characteristics, making them especially vulnerable to the harmful effects of exposure to contaminants[1]. They encounter toxic substances, such as metals, through various routes, such as food, air, water, and soil. Among children under the age of 6, the act of mouthing objects is a prevalent behavior, with infants (6-12 months) and toddlers (1-3 years) exhibiting particularly frequent and prolonged instances of mouthing. In Greek children, toys were the leading cause of medical emergencies arising from the inhalation or ingestion of non-edible foreign objects, followed by coins and jewelry[2].

The absence of regulations for specific contaminants and ineffective enforcement of existing regulations in Nigeria has resulted in potentially high levels of metals found in kindergarten books. Children may be exposed to these metals by ingesting them through mouthing, presenting significant additional risks of both carcinogenic and non-carcinogenic nature, alongside those already arising from other

sources. Toxic metals (TMs), including cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb) and nickel (Ni) have the potential to harm children's health and impede their physical and mental growth. If children are exposed to high levels of these metals, it could have negative effects on their health, such as raised cholesterol levels, decreased blood sugar, impaired kidney function, weakened bones, digestive problems, and an increased risk of cancer. Books and toys can be among the primary sources of toxic metal exposure for children[3].

Children's exposure to heavy metals like lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), selenium (Se), mercury (Hg), barium (Ba), and zinc (Zn) is often a result of these metals being added to plastic toys, kindergarten books, and jewelry. These metals are typically added to enhance product stability and to give them certain properties like softness, brightness, and flexibility. However, there is a concern that these metals can be released or migrate when children chew or suck on these items, potentially leading to long-term toxic effect[4].

Toxic exposures in children are a major concern due to several factors. These include children having a higher metabolic rate and a greater surface area to weight ratio compared to adults. Additionally, their organ systems are still immature, and their organs and tissues, such as the bone and brain are in rapid growth and development stages. All of these factors make children more vulnerable to the harmful effects of toxic substances. Children's exposure to toxic substances differs from that of adults in several ways. Children tend to consume more fluids, eat higher quantities of food and inhale more air per kilogram of body weight compared to adults. This makes them more susceptible to the effects of any toxic substances present in their environment. Children have a longer time ahead of them to potentially develop diseases with long latency periods which means that any harmful effects from toxic exposures during childhood may not manifest until many years later[5]. Young children's tendency to frequently put their hands in their mouths creates a direct pathway for toxic chemicals in toys and other products to enter their bodies. This hand-to-mouth activity, combined with the fact that children come into contact with various products throughout the day, results in multiple low-dose exposures to toxic substances on a daily basis. Furthermore, children are also exposed to chemicals present in household dust and the outdoor environment, further adding to their overall exposure to toxic chemicals[6]. The objective of this study is to assess the concentration and potential risk of certain potential toxic metals (PTM), such as lead (Pb), Cadmium (Cd), Nickel (Ni), Arsenic (As) and Copper (Cu) that can leach out from kindergarten books. The study focuses on books purchased from various markets in the South-Eastern geopolitical zone of Nigeria and simulates the effect of saliva on the leaching process. By measuring the concentrations of these metals, the study aims to evaluate the potential health risks

associated with the use of these books by children.

MATERIALS AND METHODS

Description of Study Area

The South-Eastern Geopolitical Zone of Nigeria constitutes one of the six geopolitical regions in the country, encompassing five states: Abia, Anambra, Ebonyi, Enugu, and Imo. This zone is situated in the southeastern portion of Nigeria, adjacent to the South-South and South-West regions. The area is predominantly inhabited by the Igbo ethnic group and contributes significantly to Nigeria's economic and cultural landscape. The geographical coordinates of the region generally fall between approximately 4.5°N to 7.5°N latitude and 6.5°E to 8.5°E longitude.

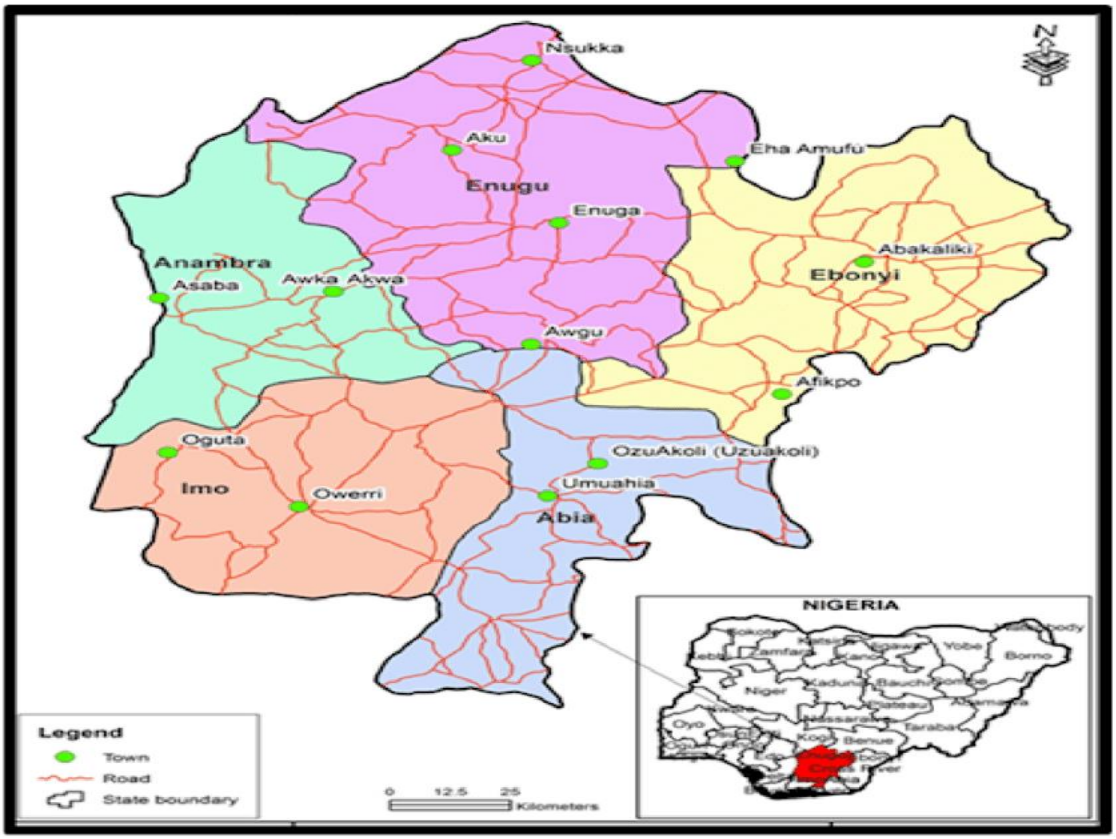

Figure 1: Map of South-Eastern Geopolitical Zone of Nigeria

Preparation of Artificial Saliva

The preparation of artificial saliva involves using materials such as albumin, methyl cellulose, sodium carboxymethyl cellulose, hydroxy-propylmethyl cellulose, potassium chloride, di-potassium hydrogen phosphate, sodium fluoride, magnesium chloride, glucose, and methyl

paraben. The process starts by dissolving albumin, cellulose, potassium chloride, potassium phosphate, and sodium fluoride in water. In a separate step, methyl paraben, magnesium chloride, and glucose are dissolved in warm water, allowed to cool, and then combined with the earlier solution. A flavoring agent is added to the final mixture.

Sample Collection and Preparation

Twenty (20) different kindergarten book samples were bought from different markets in the Eastern region of Nigeria. These books were sampled because there is a possibility of them containing higher concentration of TM. The samples were taken to the laboratory and were subjected to grinding in other to be reduced in to small fine particles. The ground samples were stored in polyethylene containers and labelled accordingly.

Toxic Metals in Kindergarten Books

The TM in Kindergarten Book Samples were analyzed by mixing 2.0 g of the sample with 20 mL of artificial saliva on a hot plate for 1 hour. After cooling, the mixture was filtered into a 50 mL volumetric flask and made up with distilled water. The filtrate was stored at 4°C for later analysis using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Cooling was essential to prevent precipitation during filtration. Samples were prepared and analyzed in triplicate to ensure result accuracy.

Bioavailability of TM in Kindergarten Books (Saline and HCl extraction)

Saline extraction as used by Weidenhame to simulate exposures obtained by mouthing behaviours was modified[7]. An exact portion of 2.0 g of the book samples were weighed and placed in conical flasks. 50 mL of the saline solution was added into the conical flasks. The Conical flask containing the sample and saline solution were placed on the shaker and agitated for 30 mins at 37°C. Simulation of the stomach phase was carried out by mixing 2.0 g of the book sample with 0.07 M standard dilute HCl in a conical flask. The solution was agitated for 2 hours at 37°C using a shaker. Supernatant were filtered into a polyethylene container and analyzed for Pb, Cd, As, Cu and Ni.

Risk Assessment Study

Due to the high frequency of mouthing of kindergarten books by children in the age category of 6 months to 1 year, risk assessment was carried out accordingly using the methodology suggested by Cui[8]. The chemical daily intake (CDI) from the saliva (saline extraction) was calculated thus:

$$CDI_{saliva} = Q_{bio} \times {}^{ED}/_{BW}$$

Where CDI_{saliva} = CDI by mouthing (µg $k^{-1}d^{-1}$), and Q_{bio} is the bioaccessible fraction of metals in the saline extraction using 10 g of sample with an area of about 10 cm^2 [9]. ED = duration of exposure and 66 minsd^{-1} was used according to Smith and Norris, for children in this

age category[10] and BW is the average body weight of children between 6 and 12 months. A weight of 9.2 kg was used[11]. The chemical daily intake from ingestion of the Kindergarten book sample (acid extraction) was calculated using

$$CDI_{ingestion} = Q_{bio} \times {}^{EF}/_{BW}$$

Where $CDI_{ingestion}$ is the chemical daily intake by ingestion, $Qbio$ is the bioaccessible fraction of metals in the 0.07 M acid extraction and EF is the exposure frequency. The EF was assumed to be 1 day.

The hazard index (HI) for oral exposure of potentially toxic metals in kindergarten books is defined as;

$$HI = \frac{CDI}{RfD}$$

Where RfD (reference dose) of the metals are Cd= 1, Pb = 4 µg $k^{-1}d^{-1}$ [12] and Ni = 10 µg $k^{-1}d^{-1}$ [8].

RESULTS AND DISCUSSION

TM in Kindergarten Book Samples

Analysis of the 20 samples for TM gave the results as seen in Table 1.

Table 1: Total concentration of TM in the kindergarten book samples analyzed (mg/kg)

Laboratory Number	As	Cd	Cu	Ni	Pb
Sample 1	16.6	10.8	83.4	8.35	60.5
Sample 2	24.8	36	59.9	8.63	111
Sample 3	14.8	13.2	39.8	7.2	101
Sample 4	14.4	13.4	90.9	11.2	72.5
Sample 5	8.45	19.2	119	4.3	107
Sample 6	3.55	23.3	32.8	3.55	50.5
Sample 7	40.7	17.7	115	11.2	36.1
Sample 8	12.2	36.6	78.1	6.28	51
Sample 9	8.85	6.96	110	4.13	37.7
Sample 10	10.5	17	119	8.1	105
Sample 11	9.41	5.43	126	7.45	83.6
Sample 12	7.68	12.2	58.4	8.93	103
Sample 13	7.63	32.5	159	9.7	88.8
Sample 14	14.8	13.1	45.3	6.88	94.4

Sample 15	14.9	12.2	17.3	6.55	107
Sample 16	6.7	34.2	30.6	2.9	52.9
Sample 17	2.85	3.21	40.3	2.85	51.3
Sample 18	38.3	1.83	81.4	6.23	62.4
Sample 19	9.38	38.9	52.2	6.35	70.8
Sample 20	6.15	34.5	9.78	6.15	70.4

Table 2: Summary of TM results of the study (mg/kg)

Metals	N	Mean ± S.D.	Range
As	20	13.6 ± 10.1	2.85 – 40.7
Cd	20	19.1 ± 12.2	1.83 – 38.9
Cu	20	73.4 ± 41.3	9.78 – 159
Ni	20	6.8 ± 2.5	2.85 – 11.2
Pb	20	75.8 ± 25.0	36.1 – 111

Table 3: Correlation study between the metal pairs

	As	Cd	Cu	Ni	Pb
As	1	-.189	.187	.487*	-.111
		.425	.430	.029	.641
Cd		1	-.154	.004	.027
			.517	.986	.909
Cu			1	.424	.003
				.062	.989
Ni				1	.266
					.256
Pb					1

*. Correlation is significant at the 0.05 level (2-tailed).

Table 4: Concentrations of the study for As, Cu and Pb after saline extraction (mg/kg)

Laboratory Number	As	Cu	Pb
Sample 1	2.03	2.08	4.93
Sample 2	ND	1.83	ND
Sample 3	ND	0.95	ND
Sample 5	ND	2.83	5.33
Sample 10	ND	2.88	4.95
Sample 11	0.53	2.60	ND
Sample 12	0.60	0.15	5.60
Sample 13	0.93	1.35	3.28
Sample 15	1.88	2.33	2.60
Sample 20	0.65	0.75	4.63

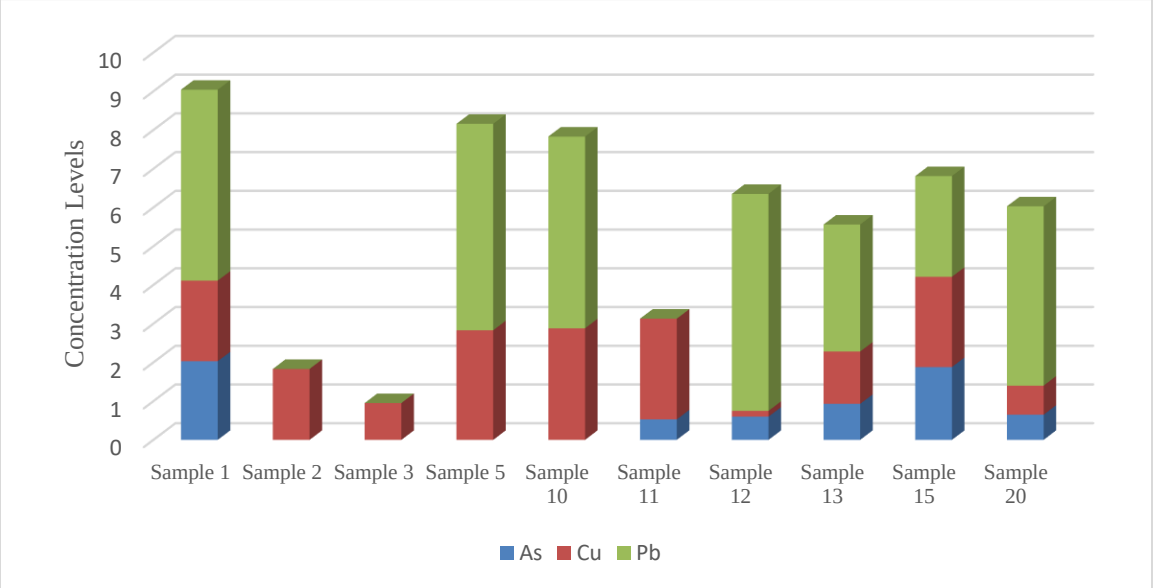

Figure 2: Graphical illustration of the study for As, Cu and Pb after saline extraction (mg/kg)

Table 5: Concentrations of the study for As, Cu and Pb after acid extraction (mg/kg)

Laboratory Number	As	Cu	Pb
Sample 1	1.15	ND	6.83
Sample 2	1.38	1.70	3.33
Sample 3	ND	1.81	7.10
Sample 5	ND	ND	5.78
Sample 10	1.78	1.68	4.35
Sample 11	ND	ND	7.00
Sample 12	3.15	1.35	3.85
Sample 13	2.73	1.33	6.70
Sample 15	2.03	ND	5.15
Sample 20	1.40	1.43	5.30

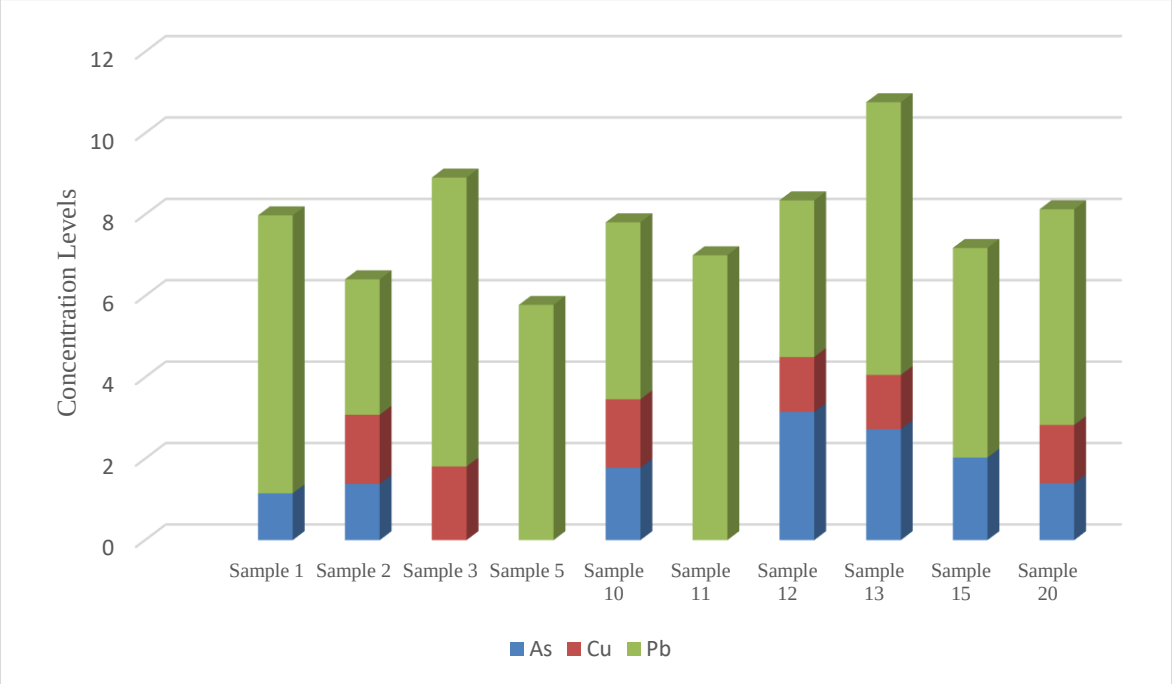

Figure 3: Graphical illustration of the study for As, Cu and Pb after acid extraction (mg/kg)

Table 6: Hazard index (HI) for oral exposure of children (6 months - 1 year) to PTM by mouthing.

Laboratory Number	**As**	**Cu**	**Pb**
Sample 1	4.85	0.05	2.95
Sample 2	-	0.44	-
Sample 3	-	0.23	-
Sample 5	-	0.68	3.19
Sample 10	-	0.69	2.95
Sample 11	1.27	0.62	-
Sample 12	1.43	0.04	3.35
Sample 13	2.22	0.32	1.96
Sample 15	4.50	0.58	1.55
Sample 20	1.55	0.18	2.77

Table 7: Hazard index (HI) for oral exposure of children (6 months - 1 year) to PTM by ingestion.

Laboratory Number	**As**	**Cu**	**Pb**
Sample 1	1.25	-	-
Sample 2	1.50	0.18	-
Sample 3	-	0.20	-
Sample 5	-	-	-
Sample 10	1.93	0.18	-
Sample 11	-	-	-
Sample 12	3.42	0.14	-
Sample 13	2.97	0.14	-
Sample 15	2.21	-	-
Sample 20	1.52	0.16	-

The TM concentrations of the kindergarten books after mixing with the prepared artificial saliva are shown in Table 1. The result showed that all the samples contained some quantity of As, Cd, Cu, Ni, and Pb. Out of the five TM studied, Pb had the highest concentrations in most of the samples except in a few cases where Cu was higher than Pb. The high concentration of Cu in some of the samples may be from the colourings since cupric substances are usually added to the ink used on the diagrams and coloured text in the kindergarten books during production to give it a brilliant looking appearance[13]. The results obtained showed that the range of concentrations of the TMs in mg/kg was as follows: 2.85-40.7, 1.83-38.9, 9.78-159, 2.85-11.2, and 36.1-111 mg/kg for As, Cd, Cu, Ni, and Pb respectively (Table 2). Correlation study of the results indicated no significant positive relationship between the metal pairs except for As and Ni pair which indicated a significant positive relationship with P-value <0.05 (Table 3).

Bioavailability Studies

The study was carried out on samples with the highest concentration of total TM by extraction with artificial saliva in other to simulate the mouthing behaviour of children and stomach acid extraction to simulate ingestion of the kindergarten books (Tables 4 and 5). The result of the saline extraction shows that the concentration of As in the saline extraction were below the detection limits in samples 2, 3, 5 and 10 whereas, Cu was detected in all the samples. Also, for samples 2, 3 and 11, Pb extract were all below the detection limit of the instrument used (Figure 2). The results of the stomach acid extraction using HCl solution showed that Pb had the highest concentration followed by As and Cu. Samples 3, 5 and 11 showed no As in the extract, while samples 1, 5, 11 and 15 showed no Cu in the extract (Figure 3). The acid extraction was carried out to check the amount of heavy metals that could leach out from these book materials when their particles find their way into the stomach of the child. The result of the concentration in mg/kg of Pb, As and Cu in the kindergarten book sample after acid extraction showed that these heavy metals can leach out in the stomach of these children and cause serious health effects when there is bioaccumulation of the metals.

Risk Assessment of TM in Kindergarten Book Samples

Risk assessment was done by calculating the hazard index (HI) from the chemical daily intake and the reference dose values of the metals. When the HI is > 1, the risk is significant, while when it is > 0.1, the risk though not significant, should not be neglected.

All the samples studied either had HI > 0.1 or >1 for As, Cu and Pb, with the exception of samples whose concentrations were below the detection limit as shown in table 5 and 6. The highest HI was observed for As. Sample 15 had an index value as high as 4.50 for mouthing (saline extraction), and 2.21 for the ingestion (acid

extraction). All the samples had an HI >1 for Pb for mouthing with the exception of sample 2, 3 and 11 while for ingestion, the concentrations were below the detection limit. The HI for As and Pb exposure were generally greater in the saline extraction than the acid extraction. Most of the samples has HI > 0.1 for Cu in both the saline and acid extraction.

CONCLUSION

This research reveals that majority of kindergarten books contain potentially toxic metals in varying concentrations which are being exposed to children and these metals may pose hazards to children's health and create a major problem in its use and disposal**.** Risk assessment from oral exposure to the metals investigated showed that exposure of children to As, Cu and Pb may present unacceptable and significant hazard risk, and these heavy metals can leach out in the stomach of these children and cause serious health effects when there is bioaccumulation of the metals.

REFERENCES

1. Miller, M. D., Marty, M. A., & Landrigan, P. J. (2016). Children's environmental health: beyond national boundaries. *Pediatric Clinics*, *63*(1), 149-165. https://doi.org/10.1016/j.pcl.2015.08.008

2. Farmakakis, T., Dessypris, N., Alexe, D. M., Frangakis, C., Petoussis, G., Malliori, M., & Petridou, T. E. (2007). Magnitude and object-specific hazards of aspiration and ingestion injuries among children in Greece. *International journal of pediatric otorhinolaryngology*, *71*(2), 317-324. https://doi.org/10.1016/j.ijporl.2006.10.021

3. Guney, M., & Zagury, G. J. (2011). Toxic chemicals in toys and children's products. *Environmental Science and Technology*, *45*(9), 3819. https://doi.org/10.1021/es200810s

4. Guney, M., & Zagury, G. J. (2012). Heavy metals in toys and low-cost jewelry: critical review of US and Canadian legislations and recommendations for testing. Environmental science & technology, 46(8), 4265-4274. https://doi.org/10.1021/es203470x

5. Becker, M., Edwards, S., & Massey, R. I. (2010). Toxic chemicals in toys and children's products: limitations of current responses and recommendations for government and industry. *Environmental science & technology*, *44*(21), 7986-7991. https://doi.org/10.1021/es1009407

6. Tripathi, R. M., Raghunath, R., & Krishnamoorthy, T. M. (1997). Dietary intake of heavy metals in Bombay city, India. *Science of the total environment*, *208*(3), 149-159. https://doi.org/10.1016/S0048-9697(97)00290-8

7. Weidenhamer, J. D., Miller, J., Guinn, D., & Pearson, J. (2011). Bioavailability of cadmium in inexpensive jewelry. *Environmental health perspectives*, *119*(7), 1029-1033. https://doi.org/10.1289/ehp.1003011

8. Cui, X. Y., Li, S. W., Zhang, S. J., Fan, Y. Y., & Ma, L. Q. (2015). Toxic metals in children's toys and jewelry: coupling bioaccessibility with risk

assessment. *Environmental pollution*, *200*, 77-84. https://doi.org/10.1016/j.envpol.2015.01.035

9. Guney, M., & Zagury, G. J. (2014). Children's exposure to harmful elements in toys and low-cost jewelry: characterizing risks and developing a comprehensive approach. *Journal of hazardous materials*, *271*, 321-330. https://doi.org/10.1016/j.jhazmat.2014.02.018

10. Smith, S. A., & Norris, B. (2003). Reducing the risk of choking hazards: mouthing behaviour of children aged 1 month to 5 years. *Injury control and safety promotion*, *10*(3), 145-154. https://doi.org/10.1076/icsp.10.3.145.14562

11. Ferguson, A., Penney, R., & Solo-Gabriele, H. (2017). A review of the field on children's exposure to environmental contaminants: A risk assessment approach. *International journal of environmental research and public health*, *14*(3), 265. https://doi.org/10.3390/ijerph14030265

12. WHO, F. A. O. (2013). Guidelines for the safe use of wastewater and food stuff: Wastewater use in agriculture. *Switzerland, Geneva*, *988*.

13. Fung, D. R., Liao, T. C., & Wang, S. H. (2010). *U.S. Patent Application No. 12/588,942*.