Second-Hand Infant Care Plastic Products Sold in Markets of Kalar City, Kurdistan Region, Iraq: Heavy Metals Contamination and Risk Assessment

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Abstract
In this study, health risk assessment and contamination have been performed of fourteen toxic heavy metals in six second-hand plastic infant care products collected from markets of Kalar city, Kurdistan region of Iraq. Second-hand infant care plastic products might impose serious health concerns if they contain high levels of heavy metals. The toxic heavy metal elements concentrations have been identified and analyzed using inductively coupled plasma optical emission spectroscopy (ICPOES, Spectro Arcos). Many of the investigated products contain considerable or high levels of the examined heavy metals according to the European Union EU safety limits for brittle, pliable, liquid and sticky toy materials. The highest level of heavy metals has been noticed was of zinc 10643.4 mg/kg in sample ST1 (183% higher than the allowable limit). High concentrations of lead Pb, mercury Hg, and chrome Cr have also detected. Statistical analysis of Pearson correlation matrix CM, and hierarchical cluster analysis HCA found significant correlations between many heavy metals and infant care samples respectively. Health risk assessment for sample ST6 identified a moderate significant hazard index regarding heavy metals of arsenic, mercury, and cobalt with HI values of 0.5652, 0.2967 and 0.1211 respectively. This work leads thus safety measure is respected in the investigated infant care samples. Furthermore, stringent procedures are needed to limit the handling and importing of such products into the markets in the future.

1. Introduction

Environmental contamination is increasingly becoming a matter of a great global issue (Oke 2004). Contamination of commercial products and foodstuffs with toxic elements is now a vital factor concerning human health (Kakimov et al. 2013; Stef and Gergen 2012). Plastic toys are objects that very often used by children and infants for playing and enjoyment. Toys and other infant care products are necessary factors during the progression of the infant’s life (Landrigan et al. 2004). Therefore the exposure to a number of toxic elements and heavy metals presented in infants are possibly greater through the mouthing of toys and non-food products (Landrigan and Goldman 2011). Many infant and child-care products may contain various harmful components such as toxic elements and heavy metals in their compositions (Becker et al. 2010). Hence the main potential source of exposure and transfer of dangerous chemicals and toxic elements to infants is through their toys (Decharat 2017; Earls et al. 2003).

Despite the fact, the heavy metals are naturally existing in soil and rocks (Marcovechio et al. 2007). Toxic elements like heavy metals are considered as the most detrimental contaminants regarding their non-biodegradable behavior (Kopp et al. 2018). They tend to accumulate in biological systems like the human body (Kim et al. 2015). Heavy metals present in the environment may involve essential and toxic heavy metals (Issa and Alshatteri 2018; Mahmood et al. 2012). The essential metals are Co, Cr, Fe, Mn, Mo, Ni, Se, Sn, V, Cu, and Zn, these metals are critical for sustaining biological life within a certain range (Nkono
and Asubiojo 1997). Accumulation of critical heavy metals in the human body also is unsafe and may cause harmful consequences (Nahar and Zhang 2012). While the toxic and non-essential heavy metals of Cd, Pb, Al, As, Ba, Hg, Be, and Ti are highly toxic and may cause chronic poisoning (Duruibe et al. 2007).

Infants or children care products that contain posing a detrimental health risk to this specific age group (Felter et al. 2015). As infants and toddlers are frequently mouthing objects for long durations (Finch et al. 2015). For example, infant’s exposure to toxic elements such as Mn, As and Cd by way of ingestion of infant care product resulted in severe cases of poisoning associated with neurodevelopment and behavioral disorders (Ciesielski et al. 2012; Rodríguez-Barranco et al. 2013). While ingestion and exposure to PVC products contain Pb may result in serious acute or chronic adverse effects may lead to death (VanArsdale et al. 2004). Moreover, a low dose of these heavy metal has various effects on the infant’s health, especially on the brain and nervous system (Lanphear et al. 2005). Exposure of infants to heavy metals in toys is not the only migratable way to their body, water and food are additional exposure risk certain toxic elements (Luca et al. 2018; Scheuplein et al. 2002). Studies on this issue showed that many infant care products were contaminated with various toxic elements such as Cd, Cu, Ni, As, Se, Hg, Cr, Zn, Co and Sb (Grynkiewicz-Bylina 2011; Korfali et al. 2013; Rebelo et al. 2015).

Recently, the raised awareness on the presence of toxic elements in infant care products provoked many regulations adopted to limit their consequences (Goldman 1998; Hervey and McHale 2004; Wigle et al. 2007). The United States consumer product safety commission (CPSC) recalled many toy or children jewelry products (Weidenhamer et al. 2011). The adopted toys and infant care safety regulations are applied for new products, whereas are not for the second-hand and older products. Although the second-hand children and infants products are an alternative choice for their cheap prices (Miller and Harris 2015). Second-hand infant care products are mostly old plastic products despite their good looking condition, likely due to the durability of synthetic polymers and paints (Turner 2018). In developed countries, Iraq, the tendency to buy re-used or second-hand stuff (Nada Abdulrahman and Faiza Kadhim 2017), child-care products are more extensively because of the economic situation.

Even though second-hand plastic infant care products are available abundantly in Iraqi markets and in homes, no study has been conducted in Iraq to investigate and assess the presence of toxic elements in second-hand children’s toys and jewelry that sold in markets. Toxic elements and metalloids, including harmful heavy metals present in these products, can cause dangerous effects for infants and toddlers. Since the current regulations and mandatory limits dealing with second-hand infant care products are not employed effectively in Kurdistan, Iraq.

The present study describes the first investigation in this field. The current work aims to determine the occurrence of toxic elements present in second-hand plastic infant care products in Iraq. Six samples of these products were taken from Iraqi markets and used to determine the concentrations of the 19 toxic elements. Selected samples were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) to assess the potential for exposure for toxic elements through ingestion.

2. Methods and Materials

2.1. Sample Collection and Preparation

Six second-hand plastic infant care samples were collected from different locations in Iraqi markets (ST1 - ST6). The tested plastic samples are infant’s teethers and pacifiers. These samples are inexpensive products, were chosen because they are widely bought by peoples and such products are most likely contain higher toxic elements concentrations (Kang and Zhu 2015). All toys samples were thoroughly cleaned to remove dust and any undesirable dirt. The samples have been milled. The grinded samples were then stored in containers and labeled and prepared for analysis.
2.2. Element Analysis in Infant Care Samples

Inductively coupled plasma optical emission spectroscopy ICP-OES, Spectro Arcos was used to analysis 14 potentially toxic elements and heavy metals. The investigated elements are Al, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, V, and Zn. The instrument operation conditions used for analysis were: Spray chamber is Scott spray; Nebulizer: crossflow; RF power/W: 1400; pump speed: 30 RPM; Coolant flow (L/min): 14; Auxiliary flow (L/min): 0.9; nebulizer gas flow (L/min): 0.8; Pre flush (s): 40; Measure time (s): 28; replicate measurement: 3; argon gas (purity ≥ 99.99); multi-elements stock solutions containing 1000 mg/L were obtained from Bernd Kraft (Bernd Kraft GmbH, Duisburg, Germany); standard solutions were diluted by several dilution into 0.1, 0.5, 2 ppm in 0.5% nitric acid as diluent.

2.3. Health Risk Assessment of Infant Care Samples

The risk assessment method of infant care samples was applied using the existing previously methods proposed by (Guney et al. 2014). Infants at this age from 6 to 12 months are frequently mouthing toys and objects (Smith and Norris 2003). For saline extraction that simulates the chemical daily intake CDI from the saliva is determined by the following:

\[
CDI_{\text{Saliva}} = \frac{(B_{\text{ac}} \times ED)}{BW}
\]

where \(B_{\text{ac}}\) is the bioaccessible quantity of an element in saliva (saline extraction) for 30 min of exposure (μg /min), ED is the daily exposure time (30 min /day), and BW is the average weight of infant’s boy which is assumed to be about 9.2 kg for 6-12 month old (U.S. EPA 2005). For this work, 10 g was selected as an average value, ED of 66 min/d was used for 6-12 months old children (Cui et al. 2015). Using specific exposure durations and the same average weight of infant’s boy for same age category: the chemical daily intake from ingestion of the toy sample (acid extraction) CDI was also calculated as follows

\[
CDI_{\text{Ingestion}} = \frac{R_{mg} \times EF}{BW}
\]

where \(R_{mg}\) is the rate of migration bioaccessible fraction of metals in the 0.07 M HCl acid extraction (μg/min), and EF is the exposure duration (min/d) assuming 1 h/d of playtime has mouthing time of 26 min/h for 6-12 months old infants (Guney et al. 2014). 10 g of the sample was considered as mentioned above. A hazard index HI for oral exposure and ingestion of elements was established as the following

\[
HI = \frac{CDI}{RfD}
\]

where RfD is the reference dose for a potentially toxic element, the RfD for toxic elements investigated in this work (μg/kg d) are Al = 750; Ba = 600; Cd = 0.5; Co = 1.4; Cr = 5; Cu = 83; Hg = 2; Mn = 160; Ni = 10; Pb = 3.6; Se = 5; Zn = 500 were adapted from (Van Engelen et al. 2009). While RfD in (μg/kg d) for As = 0.3; V = 3 were adapted from (Agency for Toxic Substances and Disease Registry (ATSDR) 2017).

To assess the accuracy of the digestion method, one selected sample material analysis was duplicated.

2.4. Statistical Analysis

Three statistical analysis techniques were performed for the concentration of the toxic element in the second-hand infant care products. Analysis of variance ANOVA was first applied to examine differences in the average concentration of the elements in infant care products. The correlations and relations between
metal concentrations in second-hand infant care products were explored using Pearson correlation matrix CM analysis. Agglomerative hierarchical clustering AHC was applied in this work to classify samples according to their content variation of toxic and heavy metal. Ward-algorithmic linkage method and Euclidean distance are the basis to conduct statistical cluster analysis. Cluster analysis was performed using XLSTAT (version 2017 for Excel 2013 software).

3. Results and Discussion

3.1. Toxic Elements Concentrations in Second-Hand Plastic Infant Care Samples

Concentrations of 14 toxic elements in the examined second-hand infant care products are shown in Table 1. The European Union EU safety limits (European Council 2009) for brittle, pliable, liquid and sticky toy material were being listed in Table 1 for comparison. The results illustrate that all samples are containing various levels of toxic elements. At first glance, it seems the sample ST1 has the highest toxic elements concentrations of Cr, Hg, and Zn that exceed the safety limits set by the European Union for migratable elements. In sample ST1, the excess percentage of concentrations of Cr, Hg, and Zn than the European Union limits are 82.69%, 87.75%, and 183.23% respectively. High concentrations of Cr exist also in samples ST2, ST3 and ST5 with excess percentages of 77.4%, 55.67% and 89.66% than European Union limit of 37.5 mg/kg respectively. Pb had concentrations in samples ST3 and ST4 by 102.35% and 98.21% respectively higher than European safety limit of 13.5 mg/kg. Other toxic elements have high concentrations but still within the European Union safety limits. There is not a clear migration limit for vanadium yet, so any presence of this toxic metal in the examined samples may be regarded as a source with a potentially harmful effect on infant health.

However, the analysis of the six second-hand infant care samples by ICP-OES proved that mostly all the 14 examined toxic elements and metals have been added in such products. Many of these elements are used in plastic products due to their stabilizing property. Where Pb has great stabilizing property if it was compared to other metals (Greenway and Gerstenberger 2010). Recently, increasing concern about the harmful effect of lead on health made many producers to use alternatives to this metal (Levin et al. 2008; Mizuno et al. 1999). Among the alternatives to reduce the use of Pb in toys production, manufacturers are now increasingly utilizing Cd (Hillyer et al. 2014). For this reason, a high concentration of Pb is always found in old plastic products (Jaksland et al. 2000). Besides Pb, the Cr high concentrations in most of the samples are probably added due to the coloring property of Cr materials such as lead chromates to paint toys and infant care products (Erkens et al. 2001). The results showed that high concentrations of Hg and Zn were found in sample ST1 as follows: 14.081 and 10643.357 mg/kg for Hg and Zn respectively. These concentrations exceed the European Union safety limits for migratable toxic elements Hg and Zn in toys that are 7.5 and 3750 mg/kg respectively. For Zn high concentration is observed in sample ST1, this element is used in infant care products as zinc borate for flame retardation (Shen et al. 2008). While Hg was generally added to PVC toys for its antifungal and antibacterial property (Delgado et al. 2011; Tulve et al. 2015). However, some other toxic elements are existing in the examined infant care samples with relatively high concentrations but they still within the limits proposed by European Union safety limits.

Table 1. Toxic elements concentrations in infant care plastic samples (mg /kg).

<table>
<thead>
<tr>
<th>Toxic elements</th>
<th>ST1</th>
<th>ST2</th>
<th>ST3</th>
<th>ST4</th>
<th>ST5</th>
<th>ST6*</th>
<th>DML (GML)</th>
<th>LOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>249.995</td>
<td>165.317</td>
<td>2</td>
<td>71.755</td>
<td>345.137</td>
<td>0.117</td>
<td>5625 (1406)</td>
<td>0.0040</td>
</tr>
<tr>
<td>As</td>
<td>0.674</td>
<td>0.919</td>
<td>0.723</td>
<td>0.473</td>
<td>0.925</td>
<td>0.006</td>
<td>3.8 (0.9)</td>
<td>0.0026</td>
</tr>
<tr>
<td>Ba</td>
<td>0.924</td>
<td>0.224</td>
<td>2.195</td>
<td>0.797</td>
<td>1.000</td>
<td>0.009</td>
<td>4500 (1125)</td>
<td>0.0044</td>
</tr>
<tr>
<td>Cd</td>
<td>ND</td>
<td>0.050</td>
<td>0.100</td>
<td>0.050</td>
<td>0.075</td>
<td>0.001</td>
<td>1.9 (0.5)</td>
<td>0.0010</td>
</tr>
</tbody>
</table>
Another strong positive correlation was observed among the elements Mn, Hg, Cu, Hg, Cu, Ni, Co, Cr, Se and V. Similarly, another strong positive correlation was observed among the elements Mn, Cu, Hg, and Zn. Weak or negative correlations between the elements are also noticed in the samples. In general, for the examined infant care samples, positive strong correlations between specific elements mean that any changing in the concentration of one of them will be followed by changes in the related elements. Otherwise, weak or no correlations between some elements existed in the samples such as Cd, Pb and Ba propose that changes in the concentration of one of these elements have no effects the concentration of the others.

Table 2. Correlation matrix (Pearson) of toxic elements in second-hand infant care samples.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Al</th>
<th>As</th>
<th>Ba</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Se</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.00</td>
<td>0.81</td>
<td>0.32</td>
<td>0.30</td>
<td>0.79</td>
<td>0.88</td>
<td>0.70</td>
<td>0.55</td>
<td>0.61</td>
<td>0.64</td>
<td>0.11</td>
<td>0.87</td>
<td>0.47</td>
<td>0.36</td>
</tr>
<tr>
<td>As</td>
<td>0.81</td>
<td>1.00</td>
<td>0.40</td>
<td>0.58</td>
<td>0.88</td>
<td>0.95</td>
<td>0.44</td>
<td>0.41</td>
<td>0.34</td>
<td>0.60</td>
<td>0.14</td>
<td>0.83</td>
<td>0.76</td>
<td>0.10</td>
</tr>
<tr>
<td>Ba</td>
<td>0.32</td>
<td>0.40</td>
<td>1.00</td>
<td>0.71</td>
<td>0.61</td>
<td>0.44</td>
<td>0.19</td>
<td>0.22</td>
<td>0.23</td>
<td>0.65</td>
<td>0.72</td>
<td>0.43</td>
<td>0.52</td>
<td>0.04</td>
</tr>
<tr>
<td>Cd</td>
<td>0.30</td>
<td>0.58</td>
<td>0.71</td>
<td>1.00</td>
<td>0.46</td>
<td>0.42</td>
<td>-0.25</td>
<td>-0.28</td>
<td>-0.32</td>
<td>0.18</td>
<td>0.73</td>
<td>0.21</td>
<td>0.35</td>
<td>-0.56</td>
</tr>
<tr>
<td>Co</td>
<td>0.79</td>
<td>0.88</td>
<td>0.61</td>
<td>0.46</td>
<td>1.00</td>
<td>0.92</td>
<td>0.70</td>
<td>0.70</td>
<td>0.64</td>
<td>0.87</td>
<td>0.28</td>
<td>0.95</td>
<td>0.85</td>
<td>0.42</td>
</tr>
<tr>
<td>Cr</td>
<td>0.88</td>
<td>0.95</td>
<td>0.44</td>
<td>0.42</td>
<td>0.92</td>
<td>1.00</td>
<td>0.63</td>
<td>0.62</td>
<td>0.58</td>
<td>0.78</td>
<td>-0.01</td>
<td>0.93</td>
<td>0.82</td>
<td>0.36</td>
</tr>
<tr>
<td>Cu</td>
<td>0.70</td>
<td>0.44</td>
<td>0.19</td>
<td>-0.25</td>
<td>0.70</td>
<td>0.63</td>
<td>1.00</td>
<td>0.95</td>
<td>0.98</td>
<td>0.80</td>
<td>-0.22</td>
<td>0.86</td>
<td>0.50</td>
<td>0.89</td>
</tr>
</tbody>
</table>
Hierarchical cluster analysis HCA identifies the similarity among clustered results of infant care samples, by showing considerable internal clusters homogeneity. From the results presented in Figure 1, the HCA dendrogram has generated three distinct clusters (groups). The similarity of infant care samples in terms of toxic elements concentrations are categorized into three principal clusters. Cluster 1, involves ST4 and ST2 samples. Cluster 2 is one sample of ST1. Cluster 3, contains samples of ST3 and ST5. The cluster classification analysis shows the samples are mainly divided on the basis of type and toxic elements concentrations. Sample ST1 was defined as an independent cluster (cluster 2), considering that the sample showed in some way different elements concentrations (high levels of Zn, Hg and Cu). In cluster 3, Samples are most likely were grouped as per low concentrations of some heavy metals in their compositions.

3.3. Risk Assessment of Heavy Metals in Infant Care Samples

In the final part of this work, risk assessment of a second-hand sample, ST6, has been conducted using a hazard index (HI) for the determined heavy metals. The sample ST6 was chosen to achieve the risk analysis because its special condition of containing liquid inside, which is easy could be transferred to the infant's mouth and then to their bodies. The special case of sample ST6 has made no need to apply ingestion and mouthing tests, the concentrations in the sample liquid have been considered for hazard index calculation. Depending on the designated values of the chemical intake and doses of the investigated heavy metals in sample ST6, the calculated HI has been classified into three groups: HI is higher than 1, the risk is significant, HI is between 1 - 0.1, the risk is moderately significant, and HI is less than 0.1, the risk is neglected (Cui et al. 2015).

Figure 1. Hierarchical cluster analysis dendrogram of second-hand infant care samples
The results of the hazard index by ingestion obtain for sample ST6 are presented in Table 3. The result shows that the majority of the toxic elements in the studied sample ST6 have a hazard index of less than 0.1. Only three toxic elements have a HI higher than 0.1 with moderate hazard risk: arsenic As, cobalt Co, and mercury Hg, which means their toxicity should not be ignored. None of the toxic heavy metals has a hazard index higher than 1. The highest hazard index HI is detected was for arsenic with a value 0.5652. After that come to Hg and Co with values of 0.2967 and 0.1211 respectively. The HI results show how unsafe second-hand infant care products are to the health of infants and reveals the need to take precautions when buying such products for infants because of their exposure to health concerns.

Table 3. Hazard indices of toxic elements in sample ST6 for infant exposure by ingestion.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>As</th>
<th>Ba</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Se</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. (mg/kg)</td>
<td>0.117</td>
<td>0.006</td>
<td>0.009</td>
<td>0.001</td>
<td>0.006</td>
<td>0.000</td>
<td>0.127</td>
<td>0.021</td>
<td>0.003</td>
<td>0.004</td>
<td>0.001</td>
<td>0.010</td>
<td>0.000</td>
<td>0.091</td>
</tr>
<tr>
<td>Rmg (μg/10g)</td>
<td>1.17</td>
<td>0.06</td>
<td>0.09</td>
<td>0.01</td>
<td>0.06</td>
<td>0</td>
<td>1.27</td>
<td>0.21</td>
<td>0.03</td>
<td>0.04</td>
<td>0.01</td>
<td>0.1</td>
<td>0</td>
<td>0.91</td>
</tr>
<tr>
<td>BW kg</td>
<td>3.307</td>
<td>0.170</td>
<td>0.254</td>
<td>0.028</td>
<td>0.170</td>
<td>0.000</td>
<td>3.589</td>
<td>0.593</td>
<td>0.085</td>
<td>0.113</td>
<td>0.028</td>
<td>0.283</td>
<td>0.000</td>
<td>2.572</td>
</tr>
<tr>
<td>CDI (μg/kg.d)</td>
<td>750</td>
<td>0.3</td>
<td>600</td>
<td>0.5</td>
<td>1.4</td>
<td>5</td>
<td>83</td>
<td>2</td>
<td>160</td>
<td>10</td>
<td>3.6</td>
<td>5</td>
<td>3</td>
<td>500</td>
</tr>
<tr>
<td>HI</td>
<td>0.0044</td>
<td>0.5652</td>
<td>0.0004</td>
<td>0.0565</td>
<td>0.1211</td>
<td>0.0000</td>
<td>0.0432</td>
<td>0.2967</td>
<td>0.0005</td>
<td>0.0113</td>
<td>0.0079</td>
<td>0.0565</td>
<td>0.0000</td>
<td>0.0051</td>
</tr>
</tbody>
</table>

**Conclusion**

In this work, 14 toxic heavy metal concentrations have been investigated in 6 different samples of second-hand infant care plastic products sold in markets in Kalar city, Kurdistan Region, Iraq. The chemical analysis of the samples showed considerable concentrations of most of the examined toxic elements according to the European Union EU safety limits (European Council 2009) for brittle, pliable, liquid and sticky toy materials. The statistical analysis using correlation matrix identified several strong positive correlations between toxic elements such as correlations between the elements Al, As, Co, Cr, Hg, Cu, and Ni. While, Pb, Ba, and Cd have no correlations with other elements. Hierarchical cluster analysis HCA categorized the infant care sample to three distinct clusters in terms of toxicity. Similar conducts have been discovered between samples ST2 and ST4 and between samples ST3 and ST5.

Bioaccessibility and risk assessment from exposure of the sample ST6 by ingestion have revealed a moderate health risk for infant exposure to arsenic As, mercury Hg, and cobalt Co respectively. It is clear that the health risk assessment performed in this study leads to paying more attention to health concerns related to the second-hand infant care products and also developing restricted programs to control dealing with such products in local markets.

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