Toxic metals in children's toys and jewelry: Coupling bioaccessibility with risk assessment

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A B S T R A C T

A total of 45 children's toys and jewelry were tested for total and bioaccessible metal concentrations. Total As, Cd, Sb, Cr, Ni, and Pb concentrations were 0.22–19, 0.01–139, 0.1–189, 0.06–84.6, 0.14–2894 and 0.08–860,000 mg kg⁻¹. Metallic products had the highest concentrations, with 3–7 out of 13 samples exceeding the European Union safety limit for Cd, Pb, Cr, or Ni. However, assessment based on hazard index >1 and bioaccessible metal showed different trends. Under saliva mobilization or gastric ingestion, 11 out of 45 samples showed HI >1 for As, Cd, Sb, Cr, or Ni. Pb with the highest total concentration showed HI <1 for all samples while Ni showed the most hazard with HI up to 113. Our data suggest the importance of using bioaccessibility to evaluate health hazard of metals in children's toys and jewelry, and besides Pb and Cd, As, Ni, Cr, and Sb in children's products also deserve attention.

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1. Introduction

Toys and jewelry for children may contain high levels of toxic metals, such as arsenic (As), antimony (Sb), cadmium (Cd), and lead (Pb). Exposure to Pb causes impairment of cognitive development in children (Jusko et al., 2008; Kaufman et al., 2014). In addition, exposure to As and Cd may cause neurodevelopmental problems and behavioral disorders in children (Rodriguez-Barranco et al., 2013). Sb is classified as a possible carcinogen to humans with similar toxic effect to As. Increase in blood cholesterol and decrease in blood sugar have been observed after exposing to elevated Sb (Gebel, 1997; Westerhoff et al., 2008). The use of metals as stabilizers in plastics, application of metal-containing paint, and recycling of contaminated plastics are the main sources of metals in toys and jewelry (Guney and Zagury, 2012; Rastogi and Pritzl, 1996).

A report that a child in the US was dead of Pb poisoning after swallowing a jewelry charm in 2006 has attracted much attention to Pb contamination in children's toys and jewelry. In a survey conducted in 2007, 43% of 139 metallic jewelry from USA was heavily contaminated with Pb, averaging 440 g kg⁻¹ (Weidenhamer and Clement, 2007a). Due to the attention to Pb in children's products, some manufacturers have turned to Cd as an alternative. Several studies reported serious Cd contamination in children's products, and the US Consumer Product Safety Commission has recalled jewelry in 2010 due to Cd contamination (Weidenhamer et al., 2011). Even with the regulation of Pb and Cd contamination in children's products, recent research still showed ongoing contamination in toys and jewelry (Guney and Zagury, 2013a,b; Hillyer et al., 2014). Take metallic toys and jewelry for example, the highest concentrations of nickel (Ni), Cd and Pb were 140, 367 and 653 g kg⁻¹, and those for As and Sb are 0.43 and 1.02 g kg⁻¹ (Guney and Zagury, 2013a). Compared with Pb and Cd, contamination by other metals received less attention, especially for chromium (Cr) and Ni. For example, chronic ingestion exposure to Cr may induce tumor in small intestine and is considered as carcinogenic (Stout et al., 2009). So, information about metal contamination in toys and jewelry is critical to ensure the safety of children's products.

It is common for young children to mouth non-food items, and the mouthing behavior frequency peaks at 6–12 month age with 39–66 min day⁻¹ (Guney and Zagury, 2014; Smith and Norris, 2003). Mouthing behavior therefore plays an important role in children's exposure to metal contamination in toys and jewelry. For example, mouth contact with toys and jewelry may cause metal mobilization into saliva and/or ingestion of small parts into stomach of children. Once ingested, part of the metals in toys and
jewelry may become bioavailable and harmful to children’s health.

Due to its advantage in low cost with no ethical concerns, in vitro bioaccessibility tests have been used to predict metal bioavailability to humans. So far, several studies investigated Pb and Cd bioaccessibility in children’s jewelry using in vitro tests (Brandon et al., 2006; Guney and Zagury, 2013a,b; Weidenhamer et al., 2011; Yost and Weidenhamer, 2008). For example, Cd bioaccessibility in 57 heavily-contaminated jewelry (>10 g kg⁻¹ Cd) was measured using artificial saliva solution and diluted HCl (Weidenhamer et al., 2011). Based on diluted HCl, in vitro gastrointestinal test (IVG), and physiologically based extraction test (PBET), the bioaccessible Cd, Cu, Ni, and Pb in 6 out of 19 metallic toys and jewelry exceed European Union (EU) safe limits for toys (Guney and Zagury, 2013b). Most studies mainly focus on Pb and Cd in metallic toys and jewelry, with little information on other metals or other types of samples, such as plastic, paper/wood, and brittle/pliable toys and jewelry. However, such information is equally important to ensure the safety of children’s product.

The overall objective of this study was to assess the health risk of 6 toxic metals (As, Cd, Cr, Ni, Pb, and Sb) through oral exposure to children’s toys and jewelry. The specific objectives were to: 1) determine total metal concentrations in 45 toy and jewelry samples; 2) measure bioaccessible metals based on two scenarios: mobilization in saliva following mouthing and solubilization in gastrointestinal tract following ingestion; and 3) characterize health risk based on bioaccessible metals in different toys and jewelry. To our knowledge, this is the first comprehensive study to investigate metal levels and health risk in all types of children’s toys and jewelry from China.

2. Materials and methods

2.1. Toy and jewelry samples

45 toys and jewelry were purchased from wholesale market, supermarket, and street vendors in Nanjing, China. During the selection, samples with lower price were preferred. This was because previous studies reported that cheaper toys and jewelry may contain higher metal levels mainly due to the recycling of contaminated materials or the lack of regulation for raw materials (Kang and Zhu, 2013; Weidenhamer and Clement, 2007a,b). The products were grouped into five categories: 13 metallic toys and jewelry (MTJ), 19 plastic toys, 3 paper/wood toys, 8 brittle/pliable toys, and 2 paint coating toys. The MTJ included low-cost jewelry and toy car made of metal, which are expected to contain high levels of metals. The plastic toys included teethers, balloon, toy cars/planes, and rattles. The brittle/pliable toys consisted of play-dough, crayon, and watercolor pen. Based on the European Union Toy Safety Directive and due to its higher chance of ingestion (European Council, 2009), brittle/pliable toys are subject to a stricter limit than MTJ and plastic toys. The paint coating was scrapped from plastic toy car and building blocks. Similar to brittle/pliable toys, paint coating from toys are also subject to a stricter limit due to its high chance of dissolution in saliva or ingestion (European Council, 2009; Guney and Zagury, 2013a).

2.2. Metal concentrations in toy and jewelry samples

Plastic and paper/wood toys were cut into small pieces (0.5 cm × 0.5 cm) by acid-cleaned knife, and brittle/pliable toys and paint coating samples were ground into powder. For all items, aliquot of ~0.5 g of sample was used for concentration measurement. Hard plastic toys, paper/wood toys and MTJ samples were disassembled into small parts, and those parts subject to child contact were sampled for measurement. Triplicates of samples were digested with HNO₃ (reagent grade, Sinopharm Chemical Reagent Co. Ltd, China) on a hot plate at temperature of 250 °C. The digestion solution was diluted by Milli-Q water, and filtrated with 0.45 μm PES filter before measuring metal concentrations by inductively coupled plasma mass spectrometry (ICP—MS, NexION 300, PerkinElmer, USA).

2.3. Bioaccessible metals based on saliva and HCl extraction

Toy and jewelry with at least one metal level reaching half of the EU limits were subjected to bioaccessibility study. Metal bioaccessibility was measured in two ways, i.e., artificial saliva extraction to simulate the mouthing behavior of children, and extraction with 0.07 M HCl to simulate ingestion into digestive tract of children. Artificial saliva was made according to unified BARGE method (UBM) (Wragg et al., 2011). The UBM assay is a physiologically-based test that mimics mouth-stomach-intestine conditions at 37 °C with the digestion enzyme and proteins under controlled pH. Bioaccessibility tests were made in triplicate and two procedure blanks were included. Similar to total concentration analysis, ~0.5 g of sample was mixed with saliva, shaken under 37 ± 2 °C for 0.5 h, and measured by ICP-MS after filtration through 0.45 μm PES filter. In order to investigate the effects of solid:liquid ratio on metal bioaccessibility, three volumes of artificial saliva, i.e., 5, 15, and 45 ml, were selected to extract metals. Extraction with 0.07 M HCl is the protocol of EU Toy Safety Directive for migration of elements (EN71-3) (European Council, 2009). Briefly, ~0.5 g of sample was added into 50 ml 0.07 M HCl, shaken under 37 ± 2 °C for 1 h, and then sit for 1 h. The extracted metals by HCl were measured by ICP-MS. The bioaccessible concentrations were calculated by dividing saliva/HCl-extracted metal mass (μg) with mass of toy (kg).

2.4. Health risk assessment of toy and jewelry

Risk assessment was conducted based on bioaccessible metal concentrations under two scenarios, i.e., artificial saliva and 0.07 M HCl extraction. Age category of 6–12 month old children was selected as the target group due to their high frequency of mouth behavior (Smith and Norris, 2003). For mobilization in saliva, the chemical daily intake (CDI) was calculated by Equation (1):

\[
\text{CDI}_{\text{saliva}} = Q_{\text{bio}} \times ED \times BW
\]

Where \(\text{CDI}_{\text{saliva}} \) = CDI by mouthing (μg kg⁻¹ d⁻¹), and \(Q_{\text{bio}} \) = bioaccessible metals in saliva extraction based on 10 g of sample for 30 min (μg). It would be more realistic to use contact area instead of toy mass to evaluate the risk through mouthing behavior. The contact area was estimated to be ~10 cm² (Guney and Zagury, 2014), and the mass based on this area can be from several grams for light toys (such as plastic samples) to couple hundred grams for metallic toys. In this study, 10 g was selected as an average value. \(ED\) = exposure duration and 66 min d⁻¹ was used for 6–12 month old children (Smith and Norris, 2003), and \(BW\) = body weight of 9.2 kg for 6–12 month old children (USEPA, 2004).

For ingestion scenario, the CDI was calculated by Equation (2):

\[
\text{CDI}_{\text{ingestion}} = Q_{\text{bio}} \times EF \times BW
\]

Where \(\text{CDI}_{\text{ingestion}} \) = CDI by ingestion (μg kg⁻¹ d⁻¹), \(Q_{\text{bio}} \) = bioaccessible metals in 0.07 M HCl extraction (μg) and 10 g was the mass of toy/jewelry ingested (Guney and Zagury, 2014), \(EF\) = exposure frequency and 1d was assumed, and \(BW\) = body weight of 9.2 kg for 6–12 month old children (USEPA, 2004).
The hazard index (HI) for oral exposure to metals in toy and jewelry was calculated through the following Equation:

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

(3)

With RfD value of Cd = 0.5, Pb = 3.6, Cr = 5, and Ni = 10 μg kg$^{-1}$ d$^{-1}$ (van Engelen et al., 2006), As = 0.3 μg kg$^{-1}$ d$^{-1}$ (ATSDR, 2013), and Sb = 0.4 μg kg$^{-1}$ d$^{-1}$ (USEPA, 1991).

2.5. Quality assurance and quality control

The detection limits for Cd, Sb, Pb, As, Cr, and Ni on ICP-MS were 1, 2, 8, 10, 44, and 71 ng L$^{-1}$, respectively. Metal concentrations in blanks from the digestion and bioaccessibility experiments were below or close to detection limit. Linear regression was performed using Sigmaplot v 11.0.

3. Results and discussion

3.1. Metal concentrations in toy and jewelry samples

Total concentrations of As, Pb, Cd, Cr, Ni, and Sb in 45 toy and jewelry samples are listed in Tables 1 and 2, and 3, with the EU safety limits being listed for comparison (European Council, 2009). When compared with limits regulated by USA and Canada, the EU limits cover more elements (17 metals instead of only Pb and Cd in USA and Canada limits) and set limits according to toy types (limit I for brittle/pliable toys and limit III for metallic and plastic toys), which represents a more realistic scenario. The EU limits include As = 47, Pb = 90, Cd = 23, Cr = 460, Ni = 930, and Sb = 560 μg kg$^{-1}$ for scraped-off toy material, which are applicable to MTJ plastic toys, and paper/wood based toys (limit III). Lower limits were set for brittle or pliable material, including brittle/pliable toys and paint coating samples, i.e., As = 3.8, Pb = 13.5, Cd = 1.9, Cr = 37.5, Ni = 75, and Sb = 45 mg kg$^{-1}$ (limit I) (European Council, 2009).

3.1.1. Metal concentrations in 13 metallic toys and jewelry

As expected, metallic toys and jewelry (MTJ) contained high levels of metals. Total Pb concentrations ranged from 1.0 mg kg$^{-1}$ to 860 g kg$^{-1}$, with 4 metallic toys and jewelry exceeding the EU limit of 90 mg kg$^{-1}$ (i.e., MTJ7: flower-shaped bracelet, MTJ8: remote toy car, MTJ9: gray bracelet, and MTJ10: yellow bracelet) (Table 1). The 31% Pb exceeding rate was not as high as those in previous studies. For example, Weidenhamer and Clement (2007a) reported that ~5% of 139 metallic jewelry samples in USA contained >600 mg kg$^{-1}$ Pb, with 24% being >900 g kg$^{-1}$. In addition, their study showed that Pb contents are high at 3.0–62 g kg$^{-1}$ in 39 high-Pb samples. The Sb contents are comparable to that in Pb-battery (30 g kg$^{-1}$), indicating that recycled Pb-battery was probably the main source of Sb in those samples (Weidenhamer and Clement, 2007b). In the current study, Sb levels in the 4 samples with high Pb contents were ND—189 mg kg$^{-1}$ and much lower than Sb content in Pb-battery, indicating that Pb was probably not from recycled Pb-battery (Table 1). Due to recalls of low-cost toy and jewelry in North America (US CPSC, 2008) and strict regulation for Pb in children’s products, Pb concentrations in low-cost toy and jewelry have been decreasing. For example, Guney and Zagury (2013b) found that Pb levels in 20 metallic toys and jewelry are 325 mg kg$^{-1}$—650 g kg$^{-1}$, which was comparable with our results.

Using Pb-contaminated material to produce toy and jewelry has decreased as manufacturers move to Cd as an alternative (Becker et al., 2010). Before 2008, large amount of Cd, e.g., 75% of Cd produced in China, has been used for Ni–Cd batteries, which are reused to produce low-cost toy and jewelry (Asian Metal Ltd. 2008). Due to the EU legislation to restrict Ni–Cd battery use and elimination of tax rebates for Cd battery in China after 2008, Ni–Cd battery production has decreased. Therefore, Cd and Ni concentrations in toy and jewelry are expected to decrease. However, in the current study, 2 and 7 metallic toys and jewelry exceeded EU limit for Cd and Ni (23 and 930 mg kg$^{-1}$) with values of 42–139 and 932–2894 mg kg$^{-1}$. It is also important to note that, for some samples such as Ni concentrations in MTJ4 and MTJ5, large variations among replicates were not avoidable even with careful operation. This was attributed to the heterogeneity in the chemical composition of different sections of a toy or jewelry. This indicated that metal contents can vary widely between parts of a toy or jewelry, as such, frequent testing is necessary when conducting safety survey of toy and jewelry for regulation purposes.

Unlike cationic metals Pb, Ni and Cd, relatively low concentrations of As (<21 mg kg$^{-1}$) and Sb (<189 mg kg$^{-1}$) were measured in metallic toys and jewelry. The results were comparable to previous report that out of 24 metallic toys and jewelry, all but 4 samples comply with EU limits (Guney and Zagury, 2013a). However, in the current study, Cr in MTJ2 (bracelet-metal chain) was at 769 mg kg$^{-1}$, which was ~2 times of the EU limit (460 mg kg$^{-1}$). Our
plastic toys may have decreased. Only PL8 (toy plane) contained elevated Pb (44 mg kg$^{-1}$) in the current study, which was much lower than those in previous results. For example, Kang and Zhu (2013) reported that 27 of 72 plastic toys from Beijing market contain >100 mg kg$^{-1}$ Pb. The low Pb contents in metallic toys and jewelry and plastic toys in our results suggested that recent Pb regulations have positive effect on the safety of children’s products. Compared to metallic toys and jewelry, plastic and paper/wood toys posed lower threat for children because of their lower metal concentrations. However, small painted pieces, such as jigsaws (PW2), which can be readily ingested, may be of concern for children. Regulation about Cr used in pigment also deserves more attention to ensure the safety of children’s products.

### 3.1.2. Metal concentrations in 22 plastic and paper/wood toys

Compared with metallic toys and jewelry, the overall metal levels in plastic (PL) and paper/wood toys (PW) were lower. For instance, the average Pb concentration in metallic toys and jewelry was 81.6 g kg$^{-1}$, which was much higher than the 3.19 mg kg$^{-1}$ for plastic and paper/wood toys. However, average Cr concentration in plastic and paper/wood toys was 279 mg kg$^{-1}$ compared to 85 mg kg$^{-1}$ for metallic toys and jewelry, indicating more Cr contamination in plastic and paper/wood toys. Four samples (i.e., PL3, PL4, PW1, and PW2) exceeded the EU limit of 460 mg kg$^{-1}$ (Table 2). The sources of Cr was unclear but may be related to Cr-containing pigments. For example, lead chromate and chromic chloride have been used as pigment to make yellow or green color (Greenway and Gerstenberger, 2010). Samples PL3 and PL4 are plastic balls with coating pigments containing Cr. For PW2, which can be readily ingested, may be of concern for children. Regulation about Cr used in pigment also deserves more attention to ensure the safety of children’s products.

### 3.1.3. Metal concentrations in 10 brittle/pliable and paint coating toys

Results showed that only 1 out of 8 brittle/pliable toys (BP) exceeded the EU safety limit for Cr with BP1 at 555 mg kg$^{-1}$ (Table 3). BP1 was a play dough set with several colors, including red, blue, white, yellow, and green. The high Cr may come from lead chromate and chromic chloride used as pigment to make yellow and green color (Greenway and Gerstenberger, 2010). Due to the larger amount and higher probability of ingestion, more strict limits are given to BP than other types such as metallic and plastic toys and jewelry. For example, the limit for Cr in BP samples is 37.5 mg kg$^{-1}$ (limit I), which is much lower than the limit for metallic and plastic toys and jewelry at 460 mg kg$^{-1}$ (limit III). However, the Cr in BP play dough was even higher than 460 mg kg$^{-1}$. Consequently, it is important to regulate the use of toxic metal such as Cr in pigment for brittle/pliable toys.

For paint coating from toys, sampling was difficult as the paint were scraped from the surface of toys, which was time-consuming and labor-intensive, and the amount obtained was generally small. Consequently, only two paint coating samples (PC) were obtained, with one sample (PC1) contained 10 mg kg$^{-1}$ Cd, exceeding the EU limit of 1.9 mg kg$^{-1}$. However, due to the difficulty of scraping paint
with children's teeth, it is expected that exposure to paint coating on toy surface may pose less threat to children.

Overall, among 45 pieces of toys and jewelry, 3, 4, 6 and 7 samples exceeded the EU limits of Cd, Pb, Cr and Ni, respectively, but none for As and Sb. Our data suggested that besides Cd and Pb, attention should also be paid to Cr and Ni based on total concentrations.

### 3.2. Metal bioaccessibility in toys and jewelry samples

Three different volumes of saliva (i.e., 5, 15, and 45 ml) were used to investigate the effect of solid:liquid ratio on metal bioaccessibility in toys and jewelry. However, there was no consistent trend observed for bioaccessible metal concentrations under three saliva volumes (Fig. 1). For example, the bioaccessible Ni in PL17 (plastic toys) increased with saliva volumes, but opposite trend was observed for Ni in PL8. Meanwhile, there was no significant difference among the three saliva volumes for Ni in BP1 (brittle/pliable toys). Similar results were obtained for other metals in toys and jewelry samples (data not shown). Due to the inconsistent effect of saliva volume on the metal bioaccessibility, 15 ml of saliva used by UBM method was selected for extraction.

Bioaccessible metals (%) under both saliva and 0.07 M HCl extraction are shown in Fig. 2 with individual values being listed in Table 4. For all samples under saliva extraction, there was no exceedance of the EU safety limits for all 6 metals with only elevated Ni concentrations being observed. The bioaccessible Ni concentrations in MTJ3 and MTJ5 were 261 and 67 mg kg\(^{-1}\), which were \(-30\%\) and 10\% of the EU safety limit of 930 mg kg\(^{-1}\) (Table 4). Our results were similar to previous report by Guney and Zagury (2014) who used saliva extraction from the DIN method to study metal bioaccessibility in metallic toys and jewelry. The bioaccessible Ni concentrations in our study ranged from ND to 261 mg kg\(^{-1}\) (Table 4) compared to ND–391 mg kg\(^{-1}\) reported by Guney and Zagury (2014). In addition, bioaccessible Cd concentrations were ND–0.93 mg kg\(^{-1}\) (Table 4), which was lower than the ND–5.30 mg kg\(^{-1}\) reported by Guney and Zagury (2014). The lower Cd bioaccessibility in our samples was consistent with its lower total Cd concentrations (Table 1).

However, among all samples, plastic toy PL5 showed the highest bioaccessible Cd concentration at 0.93 mg kg\(^{-1}\) (Table 4). When compared to metallic toys and jewelry, plastic toys have seldom been subject to bioaccessibility study due to their much lower metal levels. Our result suggested that, even though the total metal levels in plastic toys may be low, the risk of metals from exposure to plastic toys cannot be ignored. For Pb, the bioaccessible concentrations in saliva were ND–0.64 mg kg\(^{-1}\), similar to those of Guney and Zagury (2014).

When looking into four MTJ samples with the highest total Pb concentrations (MTJ7, 8, 9, and 10), the bioaccessible Pb concentrations were much lower at 0.002–0.64 mg kg\(^{-1}\). Those four samples were composed of Pb-containing metal/alloy plated with non-Pb materials, which may inhibit Pb mobilization into artificial

### Table 3

<table>
<thead>
<tr>
<th>Label</th>
<th>Description</th>
<th>As (mg kg(^{-1}))</th>
<th>Pb (mg kg(^{-1}))</th>
<th>Cd (mg kg(^{-1}))</th>
<th>Cr (mg kg(^{-1}))</th>
<th>Ni (mg kg(^{-1}))</th>
<th>Sb (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP1</td>
<td>5 color play dough</td>
<td>ND(^{a})</td>
<td>ND</td>
<td>ND</td>
<td>555 ± 141 (I)</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BP2</td>
<td>Oil crayon set</td>
<td>1.1 ± 0.13</td>
<td>ND</td>
<td>0.21 ± 0.063</td>
<td>24.6</td>
<td>8.2 ± 0.18</td>
<td>4.1</td>
</tr>
<tr>
<td>BP3</td>
<td>Color paint</td>
<td>ND</td>
<td>ND</td>
<td>0.12 ± 0.006</td>
<td>3.72</td>
<td>ND</td>
<td>3.6</td>
</tr>
<tr>
<td>BP4</td>
<td>12 color Crayon</td>
<td>0.22 ± 0.067</td>
<td>0.68 ± 0.28</td>
<td>0.077 ± 0.028</td>
<td>0.97 ± 0.031</td>
<td>0.60 ± 0.031</td>
<td>ND</td>
</tr>
<tr>
<td>BP5</td>
<td>24 color Crayon</td>
<td>0.17 ± 0.039</td>
<td>0.68 ± 0.15</td>
<td>0.18 ± 0.0084</td>
<td>1.9 ± 0.074</td>
<td>0.72 ± 0.11</td>
<td>ND</td>
</tr>
<tr>
<td>BP6</td>
<td>12 color pencil</td>
<td>0.26 ± 0.066</td>
<td>3.9 ± 0.35</td>
<td>0.16 ± 0.015</td>
<td>26 ± 2.3</td>
<td>15 ± 1.1</td>
<td>ND</td>
</tr>
<tr>
<td>BP7</td>
<td>12 color pencil</td>
<td>1.2 ± 0.072</td>
<td>2.0 ± 0.11</td>
<td>0.18 ± 0.023</td>
<td>8.4 ± 0.42</td>
<td>3.1 ± 0.25</td>
<td>ND</td>
</tr>
<tr>
<td>BP8</td>
<td>12 color pencil</td>
<td>ND</td>
<td>0.11</td>
<td>ND</td>
<td>0.90</td>
<td>0.59</td>
<td>ND</td>
</tr>
<tr>
<td>PC1</td>
<td>Black paint on toy car</td>
<td>ND</td>
<td>ND</td>
<td>10 ± 1.4</td>
<td>8.2</td>
<td>33 ± 5.2</td>
<td>0.61</td>
</tr>
<tr>
<td>PC2</td>
<td>Blue paint on toy bricks</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>16</td>
<td>65</td>
<td>18 ± 4.9</td>
</tr>
</tbody>
</table>

**Average** | 0.32 | 0.75 | 1.09 | 64.6 | 12.7 | 2.64 |

\(^{a}\) Values are the European Union migration limits for toy safety of limit (I).

\(^{b}\) ND 1/4 not detected.

\(^{c}\) Bold values indicate total concentrations exceeding EU migration limits.

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**Table 4**

Total metal concentrations in brittle/pliable toys (BP) and paint coating from toys (PC) (mg kg\(^{-1}\), average ± standard deviation).

<table>
<thead>
<tr>
<th>Label</th>
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<td>ND</td>
<td>0.12 ± 0.006</td>
<td>3.72</td>
<td>ND</td>
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<tr>
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<td>2.0 ± 0.11</td>
<td>0.18 ± 0.023</td>
<td>8.4 ± 0.42</td>
<td>3.1 ± 0.25</td>
<td>ND</td>
</tr>
<tr>
<td>BP8</td>
<td>12 color pencil</td>
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<td>0.11</td>
<td>ND</td>
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**Average** | 0.32 | 0.75 | 1.09 | 64.6 | 12.7 | 2.64 |

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**Fig. 1.** Bioaccessible Ni and Cr concentrations in selected toys and jewelry extracted by different volumes of artificial saliva based on Unified BARGE Method.
saliva. However, even much lower than the total Pb concentrations, Pb mobilization by saliva may still be a concern from the aspect of children cognitive development. The safe blood Pb concentration for children’s intelligence quotient (IQ) was set as 10 μg l⁻¹. However, the IQ of 172 children at ages of 0.5–5 year old was decreased by 7.4 point as blood Pb level increases from 1 to 10 μg l⁻¹ (Canfield et al., 2003). Therefore, there is probably no safe level for children blood Pb level and Pb migration from toys to saliva still needs more attention.

It is expected that bioaccessible metal concentrations extracted by 0.07 M HCl were greater than those by saliva (Table 4). For example, bioaccessible Pb extracted by 0.07 M HCl were ND–2.43 mg kg⁻¹, which was significantly greater than ND–0.64 mg kg⁻¹ by saliva (Table 4). Unlike the low Ni bioaccessibility reported by Guney and Zagury (2013b, 2014), elevated bioaccessible Ni was observed in this study. Bioaccessible Ni concentration in MTJ3 was 1039 mg kg⁻¹, exceeding the EU limit of 930 mg kg⁻¹. In addition, for MTJ4 and MTJ5, bioaccessible Ni

![Fig. 2. Bioaccessibility of metal extracted by artificial saliva and 0.07 M HCl. Bioaccessibility (%) was calculated by dividing bioaccessible metal concentrations by total concentrations. Boxes represent the 25th to 75th percentiles, solid lines in boxes are the median values, small squares are mean values, error bars represent the 5th and 95th percentiles, and cross symbols represent the 1st and 99th percentiles.](image-url)
concentrations were elevated at 159 and 33 mg kg\(^{-1}\). For Cr, its bioaccessibility in MTJ12 was 423 mg kg\(^{-1}\), close to EU limit of 430 mg kg\(^{-1}\) (Table 4). However, bioaccessible Cr concentration (423 mg kg\(^{-1}\)) was much higher than its total Cr at 26.9 mg kg\(^{-1}\) (Table 1). The abnormal result was probably due to the heterogeneity of chemical composition in different parts of a given toy or jewelry, which was supported by the large standard deviations in total metal concentrations in some samples (such as Ni in MTJ5, Table 1). The bioaccessible values for other metals were well below the EU safe limit.

To compare bioaccessibility among different metals, bioaccessible concentrations were divided by total concentrations (Fig. 2). The mean bioaccessible extracted by saliva and HCl were 2.57 and 6.45% (Ni), 7.59 and 8.56% (Cd), 1.59 and 13.4% (Sb), 1.78 and 2.55% (Cr). The mean bioaccessible metal concentration to assess the health risk through exposure and jewelry samples. Therefore, it is important to use bioaccessible metal concentration to assess the health risk through exposure from ATSDR (2013), van Engelen et al. (2006), and USEPA (1991). The risk is considered unacceptable at HI >1 and should not be neglected when HI >0.1. The HI results based on bioaccessible metals by saliva are listed in Table 5, with samples showing HI >0.1 for all 6 metals. There were 9 samples with HI >1, which may present risk to children in terms of As, Cd, Cr, Ni, and Sb exposure. High HI values were observed in MTJ3 and MTJ4 (bracelet-chain and pendant) and MTJ5 (jewelry metal pendant) for Ni with HI being 62, 7.4, and 16, in PL5 (plastic animal figurine) for Cd with HI of 4.4, and in BP1 (color toy bricks) for As with HI of 3.5. In addition, HI >1 was observed for As in BP3 and PC2, Cr in BP1, BP2, and BP3, Cd and Ni in MTJ7, and Sb in PL17 (Table 5). Furthermore, HI = 0.1 for As, Cd, Cr, Pb, and Ni in many samples, which can still be of concern. However, the high risk (HI > 1) for As exposure in BP1, BP3, and PC2 should be considered with caution. The fact that bioaccessible concentrations by saliva (Table 4) were higher than the corresponding total As concentrations in these samples (Table 3) indicated the high sample heterogeneity. Nevertheless, it can be concluded that children's exposure to toys and jewelry via saliva may cause unacceptable hazard risk especially in terms of Cd, Cr, and Ni.

In addition to saliva, HI values based on bioaccessible metal concentrations extracted by 0.07 M HCl are listed in Table 5. Similar to saliva, there were several samples with higher bioaccessible than total concentrations. For instance, As in MTJ5, PL5, PW1, PW2, BP1, BP3, and PC2 in MTJ12, Sb in MTJ7 and MTJ8. Besides the abnormal values, very high HI values were observed for Ni at 113 and 17.3 in MTJ3 and MTJ4. Meanwhile, unacceptable risk was also observed for some other products with HI >1 for As in MTJ3 and PL17, Cd in PL5, Cr in MTJ2, Ni in MTJ5, and Sb in PC2. Therefore, it can be suggested that exposure to some toys and jewelry via ingestion may cause unacceptable hazard risk to children.

However, there were several concerns about how HI is calculated. In previous bioaccessibility tests, entire sample was used with different masses depending on toys and jewelry (Guney and Zagury, 2013a,b; Yost and Weidenhamer, 2008). The mass of toys

### Table 5

<table>
<thead>
<tr>
<th>Label</th>
<th>Description</th>
<th>As (Saliva)</th>
<th>Pb (HCl)</th>
<th>Cd (Saliva)</th>
<th>Cr (HCl)</th>
<th>Ni (Saliva)</th>
<th>Sb (HCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTJ2</td>
<td>Bracelet with metal chain</td>
<td>0.30</td>
<td>0.51</td>
<td>0.10</td>
<td>0.04</td>
<td>0.22</td>
<td>0.17</td>
</tr>
<tr>
<td>MTJ3</td>
<td>Bracelet w/metal chain</td>
<td>0.42</td>
<td>1.20</td>
<td>0.09</td>
<td>0.15</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>MTJ4</td>
<td>Bracelet w/metal chain</td>
<td>0.08</td>
<td>0.44</td>
<td>0.07</td>
<td>0.01</td>
<td>0.06</td>
<td>0.89</td>
</tr>
<tr>
<td>MTJ5</td>
<td>Metal pendant</td>
<td>0.26</td>
<td>2.25</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>MTJ6</td>
<td>Metal toy car</td>
<td>0.24</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>MTJ7</td>
<td>Flower-shaped bracelet</td>
<td>0.34</td>
<td>1.52</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MTJ8</td>
<td>Remote metal toy car</td>
<td>0.17</td>
<td>0.11</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MTJ9</td>
<td>Gray bracelet</td>
<td>0.42</td>
<td>0.15</td>
<td>0.20</td>
<td></td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>MTJ10</td>
<td>Yellow bracelet</td>
<td>0.06</td>
<td>0.23</td>
<td>&lt;0.01</td>
<td></td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>MTJ11</td>
<td>Yellow bracelet</td>
<td>0.06</td>
<td>0.23</td>
<td>&lt;0.01</td>
<td></td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>MTJ12</td>
<td>Silver bracelet</td>
<td>0.28</td>
<td>0.07</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.29</td>
<td>0.19</td>
</tr>
<tr>
<td>PL3</td>
<td>Plastic ball</td>
<td>0.61</td>
<td>0.06</td>
<td>&lt;0.01</td>
<td></td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>PL4</td>
<td>Plastic ball with spine</td>
<td>0.10</td>
<td>0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td>PL5</td>
<td>Animal figurine</td>
<td>0.10</td>
<td>1.24</td>
<td>0.01</td>
<td>0.02</td>
<td>4.43</td>
<td>2.50</td>
</tr>
<tr>
<td>PL8</td>
<td>Toy plane</td>
<td>0.69</td>
<td>0.42</td>
<td>0.03</td>
<td>0.18</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>PL9</td>
<td>Toy car</td>
<td>0.04</td>
<td>0.43</td>
<td>0.01</td>
<td>0.09</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>PL17</td>
<td>Orange colored rattle</td>
<td>0.66</td>
<td>3.25</td>
<td>0.11</td>
<td>0.06</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>PW1</td>
<td>Educational cards</td>
<td>0.03</td>
<td>9.48</td>
<td>0.14</td>
<td>0.07</td>
<td>0.12</td>
<td>0.05</td>
</tr>
<tr>
<td>PW2</td>
<td>Paper-based jigsaws</td>
<td>0.32</td>
<td>7.91</td>
<td>0.73</td>
<td>0.01</td>
<td>0.16</td>
<td>0.13</td>
</tr>
<tr>
<td>BP1</td>
<td>Play dough set of five colors</td>
<td>3.51</td>
<td>1.72</td>
<td>&lt;0.01</td>
<td>0.05</td>
<td>0.03</td>
<td>2.55</td>
</tr>
<tr>
<td>BP2</td>
<td>Oil crayon set</td>
<td>0.77</td>
<td>1.68</td>
<td>0.01</td>
<td></td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>BP3</td>
<td>Color paint</td>
<td>1.48</td>
<td>4.35</td>
<td>0.03</td>
<td>0.05</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>PC1</td>
<td>Black colored paint on toy car</td>
<td>0.32</td>
<td>&lt;0.01</td>
<td>0.03</td>
<td>0.07</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>PC2</td>
<td>Blue colored paint on toy bricks</td>
<td>2.58</td>
<td>18.7</td>
<td>0.38</td>
<td>0.08</td>
<td>0.18</td>
<td>0.36</td>
</tr>
</tbody>
</table>

**Note:**

- **a** Ratio of chemical daily intake to reference dose Cr RfD was selected at 5 and 0.9 µg kg\(^{-1}\) d\(^{-1}\) for acute toxic exposure (i.e., HCl extraction, van Engelen et al., 2006) and chronic toxic exposure (i.e., saliva extraction, ATSDR, 2013).
- **b** Bold values indicate HI values higher than 1.

### 3.3. Hazard index (HI) of metals in toys and jewelry based on bioaccessibility

Hazard index (HI) is commonly used in risk assessment. It is calculated by dividing the chemical daily intake (CDI) by RfD values.
and jewelry ingested was 10 g in the current study. The estimation seems reasonable for MTJ, but may overestimate for much lighter toy (such as plastic toy). Similarly, sample mass of 10 g was selected to calculate the HI for exposure through saliva mobilization. However, it was more realistic to assess the risk based on contact surface area instead of sample mass, and the contact area should be age and toy specific. Therefore, there is a need to improve exposure estimation such as mouth contact area and ingestion mass. There are also some uncertainty in RfD values. The RfD values for some metals are based on total amount of intake, including uptake from toy and other sources (such as water, food, and incidental ingestion of soil). However, the value from other sources usually cannot be accurately estimated, therefore calculation of HI using total RfD may underestimate the risk. Another concern was Cr speciation. The RfD value used for Cr HI calculation was based on hexavalent Cr(VI), which is much more toxic than trivalent Cr(III). The health risk from Cr exposure may be overestimated if Cr(III) coexists with Cr(VI). Therefore, Cr speciation in dilute HCl and saliva extraction needs to be investigated.

4. Conclusion

This study assessed levels of six toxic metals (As, Pb, Cd, Cr, Ni, and Sb) in different toys and jewelry, including metallic, plastic and paper/wood, brittle/pliable and paint coating. Contamination of Pb and Cd in metallic toys and jewelry is known. In addition, toys and jewelry were also a source of Ni and Cr exposures for children. Health risk was assessed based on bioaccessible metal concentrations under two scenarios, i.e., saliva extraction (simulating mouthing) and dilute HCl extraction (simulating ingestion). High risk (HI > 1) was observed for As, Cd, Cr, Ni, and Sb in some toys and jewelry, especially high for Ni with HI of 113.

In risk assessment from oral exposure to metals in toys and jewelry, variability and uncertainty for some exposure parameters (i.e., mouthing contact area and mass ingested) need more investigation. Meanwhile, Cr speciation in saliva/dilute HCl extracts is important for accurate estimation of Cr exposure from toys and jewelry. It should be noted that the exposure duration in bioaccessibility tests (30 min for saliva and 1–2 h for dilute HCl extraction) may not be reasonable. This is because longer time is possible for toys and jewelry to stay in gastrointestinal tract, i.e., transit time for foreign objects in children’s digestive tract averaged at 6 d (Macgregor and Ferguson, 1998) and therefore 24 h HCl extraction is recommended by U.S. Consumer Product Safety Council.

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References

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