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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, 0.06–846, 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.

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 neurodevelopment problems and behavioral disorders in children (Rodríguez-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

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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 venders 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 from 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 playdough, 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 HNO_3 (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):

$$CDI_{saliva} = Q_{bio} \times ED \div BW \tag{1}$$

Where CDI_{saliva} = CDI by mouthing (μg kg^{-1} d^{-1}), and Q_{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 moth behavior. The contact area was estimated to be ~10 cm^2 (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):

$$CDI_{ingestion} = Q_{bio} \times EF \div BW \tag{2}$$

Where $CDI_{ingestion}$ = CDI by ingestion (μg kg^{-1} d^{-1}), Q_{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).