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Phthalates in soft glass (a soft transparent PVC plastic sheet used extensively in household and public place in developing countries in recent years): Implication for oral exposure to young children

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HIGHLIGHTS

- DEHP is the main plasticizer in soft glass (or crystal plate), a soft PVC sheet.
- DEHP accounts for more than 50% by weight of the transparent soft glass.
- DEHP could leach out of soft glass to the olive oil and pork skin during contact.
- Estimated DEHP exposure dosages would not pose immediate health hazard to children.

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ABSTRACT

It has been several years that a soft transparent polyvinyl chloride (PVC) plastic sheet, commonly known as “soft glass”, or “crystal plate” in China and other developing countries, has quietly and gradually found extensive applications. This material has widely replaced cloth and glass as table cover in household and office, and replaced cloth as door drape in public place in China. In this study, the concentration of plasticizer used in soft glass and the migration of the plasticizer from soft glass to olive oil and porcine skin during contact were determined. The oral exposure of young children to the plasticizer from soft glass was estimated for the first time. Two exposure routes, one via ingestion of contaminated food, the other via mouthing of contaminated hand, were considered. It is found that Di(2-ethylhexyl) phthalate (DEHP) is the major plasticizer used in soft glass, which could leach out of the material and migrate easily to the olive oil and porcine skin during contact. A rough estimation of oral exposure for young children to DEHP from soft glass was 126 μg/person/d, which would be converted to 12.6 μg/kg bw/d and 7.9 μg/kg bw/d, for body weight of 10 kg and 16 kg, respectively. The estimated exposure dosages would not pose immediate health hazard to the children. The implications of these dosages were also discussed.

1. Introduction

Some plastics use plasticizer to modify their flexibility. Phthalate (or phthalic acid ester) has been one of the most important plasticizers. The global production of phthalates in 2010 was 4.9 million tons and accounted for 84% of the total plasticizer production (Emanuel, 2011). Among them, the most common phathalate is di (2-ethylhexyl) phthalate (DHEP), one of the major plasticizers for PVC material, which could be used typically as much as 40% by weight of the products (Agency for Toxic Substances and Disease Registry, 2002), and accounts for roughly 50% of all the plasticizers used in PVC (Murphy, 2001). But, there have been reports showing much higher DEHP levels in PVC products, which could be as high as 80% (Report on Carcinogens).

Due to their ubiquity and huge production, health and environmental effects of phthalates have been studied extensively. Increasing adverse effect evidences have been accumulated. Animal studies indicate that some phthalates have endocrine-disrupting properties. For example, di-*n*-butyl phthalate (DnBP), diisobutyl phthalate (DiBP), butylbenzyl phthalate (BBP) and DEHP have all been shown to cause adverse health effects on development of the male reproductive system (Mylchreest et al., 1998; Foster et al., 2001; Akingbemi et al., 2001, 2004; Borch et al., 2006). The

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metabolites of DEHP are even more toxic than DEHP itself (Richburg and Boekelheide, 1996; Horn et al., 2004; Fan et al., 2010; Piche et al., 2012). Studies of toxic effects of phthalates on human are difficult to conduct hence limited. Several extensive reviews have published and often inconclusive (Hauser and Calafat, 2005; Jakkola and Knight, 2008a; Kamrin, 2009). Because of their endocrine-disrupting properties, the adverse effects of phthalates on human infants and young children are particularly concerning. Some epidemiologic studies do support the results from animal studies (Colón et al., 2000; Duty et al., 2003; Swan et al., 2005; Pant et al., 2008). Some studies also indicate that phthalate exposure in the home environment results in increase of adverse effects on airways and immunologic system (Koralik et al., 2008; Deutschle et al., 2008; Bornehag et al., 2004, 2005; Jakkola and Knight, 2008b). There have been extensive reviews of DEHP by the US Department of Health and Human Services (Agency for Toxic Substances and Disease Registry, 2002) and the European Union (European Commision, 2008).

As phthalates are not chemically bound to plastics, they might migrate and leach out from the polymers with time. There have been huge volumes of studies on migration and leaching of phthalates from commercial products (Guart et al., 2014; Kimberly et al., 2013; Rose et al., 2012; Earls et al., 2003). Subsequently, phthalates have been found in indoors and outdoors air (Otake et al., 2001; Rudel et al., 2003; Ma et al., 2014), natural water (Penalver et al., 2000; Suzuki et al., 2001; Do Nascimento Filho et al., 2003), and soil (Fauser and Thomsen, 2002). Due to these increasing evidences of health and environmental effects, certain phthalates including DEHP have been banned for children's toys in European Union (EU, 2005), the United States (United States Consumer Pr, 2008), and Canada (HPA canada, 2010).

In China and some other developing countries, there has been a quiet trend for thick soft transparent PVC sheets to be used for workplace and household decoration, thanks to their transparency, flexibility, relatively light weight, and inert character. These transparent PVC sheets with 1–2 mm in thickness are usually called “soft glass” or “crystal plate” by general public. Soft glass and its advanced version (with decorative pattern and color) have been widely used as table cover at home and in office. They are also used extensively as assembled door drapes to insulate the stores, restaurants, or office buildings during winter and summer. While these soft glass products are flexible PVC materials which have been used ubiquitously at home and public places in recent years in China, to the best of our knowledge, they have not been investigated for phthalate content and phthalate exposure for their applications.

Four soft glass products were purchased from retail stores. Another used soft glass was also collected. Phthalates were extracted from these products with hexane. The main goal of this research was to estimate the possible oral exposure of young children to phthalate from soft glass. For this purpose, two exposure scenarios were simulated. Soft glass was soaked in olive oil as food being contaminated. Porcine skin was rubbed against soft glass as hand being contaminated. Afterwards, phthalates were extracted from the olive oil, and porcine skin using methanol, respectively.

2. Materials and methods

2.1. Sample collection

Four transparent or semi-transparent (with different color and decorative patterns) soft glass sheets (Table 1) were purchased from retail stores. They were produced by three different manufacturers. The fifth soft glass was an old transparent sheet used as table cover for four years with unknown brand. All the products were cleaned with detergent, rinsed with double distilled water and air-dried overnight before experiment.

2.2. Standards and reagents

A mixture standard with 16 phthalates and a deuterated DEHP standard (DEHP-d4) were purchased from ANPEL Laboratory Technologies (Shanghai, China). The 16 phthalates include dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), di-n-butyl phthalate (DnBP), Bis(2-methoxyethyl) phthalate, Bis(4-methyl-2-pentyl) phthalate, Bis(2-ethoxyethyl) phthalate (DEEP), Diamyl phthalate (DAP), Di-n-hexyl phthalate, Benzyl butyl phthalate, Bis(2-butoxyethyl) phthalate (DBEP), Bis(2-ethylhexyl) phthalate (DEHP), Dicyclohexyl phthalate, Diphenyl phthalate, Di-n-octyl phthalate (DnOP), Diisononyl phthalate (DiNP). Hexane and methanol were obtained from Sigma-Aldrich. All standard solutions and spiking solutions were prepared in hexane.

2.3. Phthalate contents in the soft glass

All the soft glass products were cut into small pieces (about $1 \times 1\ mm^2$). Approximately 0.3 g of each sample in triplicate was weighed into a 20-mL glass vial (with silicone septum) using an analytical balance with a precision of $\pm$ 0.0001 g. Subsequently, each sample was spiked with 500 mg DEHP-d4, and left for 24 h to equilibrate. The extraction method was to mix the spiked sample with 3 mL hexane by ultrasonication at 100 W for 1 h at 50 °C. Afterwards, the hexanes were collected and diluted accordingly for GC-MS analysis.

2.4. Phthalates migration into olive oil from soft glass

The soft glass product #1 was chosen for the phthalate migration behavior study henceforward. One piece of the soft glass with rectangular shape ($1 \times 2\ cm^2$) and 3 mL olive oil in triplicate were added to a 20-mL vial, and left for 5, 10, 15, and 30 min, respectively. The average weight of the soft glass piece was 0.377 g. Then, the soft glass was carefully removed from the vial with tweezers. Subsequently, the olive oil was spiked with 500 mg DEHP-d4, and left for 15 min to equilibrate. Methanol was used to extract phthalates from the treated oil. The extraction method was to add 3 mL methanol into the oil, followed by shaking vigorously for 10 min and centrifugation at 1000 rpm for 10 min. The upper clear layer after centrifugation was collected and diluted accordingly for GC-MS analysis.

2.5. Phthalate migration to porcine skin from soft glass

Fresh sliced porcine skin was purchased from a supermarket in Zhengzhou, China. The skin was carefully separated from subcutaneous fat, cleaned with soap, and left air-dry for 10 min. For phthalate migration experiment, the soft glass was cut to rectangular shape (4×10 and $4 \times 20\ cm^2$). Their average weights were 7.31 and 14.72 g, respectively. The cleaned porcine skin was also cut to rectangular shape ($3 \times 30\ cm^2$). In order to simulate the daily contact situation, each piece of the porcine skin in triplicate was pressed gently against one piece of soft glass while wrapped tightly on the palm of one researcher's hand, and then slid from one end of the plate to the other along the 10 or 20 cm side. One piece of porcine skin was slid against a clean glass surface as a blank. After the sliding was repeated 1, 4, 10, 20, and 40 times, respectively, the contacted part of the porcine skin was cut to small pieces of square shape ($1 \times 1\ cm^2$). Each piece was added into a 20-mL vial for